THE SOLVENT EXTRACTION AND ION EXCHANGE REMOVAL OF As, Sb AND Bi FROM COPPER REFINING ELECTROLYTES

Final Report

by

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Executive Summary

There were two primary objectives in this study. The first objective was to survey the scientific and technical literature and determine what is known about the solvent extraction or ion exchange removal of arsenic, antimony and bismuth from acid electrolytes. This survey was supplemented by direct contact with reagent suppliers. The second objective was to perform laboratory scale research on reagents identified as the most promising in the literature search. Each reagent was evaluated for the potential extraction of arsenic, antimony and bismuth.

The following conclusions may be made following this survey of solvent extractants and ion exchangers.

1. Solvating extractants are capable of e[illegible]ing arsenic from copper refinery electrolytes. The strength of the extractant for arsenic removal is linked to the strength of the extractant for acid extraction. Tri-butyl-phosphate is the most selective for arsenic over acid. Cyanex 923 is the strongest arsenic extractant identified in this study.

2. M2EHPA is a very good extractant for antimony and bismuth. Complete stripping of antimony and bismuth was demonstrated. The effective use of this reagent may be limited by reagent solubility in the aqueous phase and by the rate of hydrolytic degradation. Both of these issues should be discussed further with Albright and Wilson, the marketer of this reagent.

3. Hydroxamic acid extractants are very selective for arsenic, antimony and bismuth. Unfortunately, it is difficult to strip these species from the hydroxamic acid reagent after loading. These reagents are also prone to hydrolytic/oxidative degradation. Further development is required.

4. Kelex 100 is a promising reagent for antimony extraction. Unfortunately, in this work, a third phase developed during the studies with Kelex 100. Further investigations of antimony extraction and third phase appearance are required.

5. UR-3300 is selective for antimony and bismuth and can be stripped using 6M HCl. This resin is in use in a number of Japanese refineries, apparently with good success. Experiments included in this study confirmed the utility of this reagent.

6. C-467 is selective for antimony and bismuth and appears to be superior to UR-3300. These resins have similar functional groups. However, C-467 loaded antimony and bismuth to higher levels during standard tests. Breakthrough of antimony and bismuth did not occur until approximately the 100 bed volume mark.

7. TN-2328 is selective for antimony and loads bismuth weakly. However, this resin was inferior in performance to both UR-3300 and C-467. This resin falls in the developmental category. As such, it may be possible for Sherex to improve its functionality so that better performance is achieved.

Further study of the most promising reagents is warranted. Additional work should involve the use of plant solutions.

Table of Contents

1 INTRODUCTION 1

2 INFORMATION SURVEY 4
2.1 THE CHEMISTRY OF ARSENIC, ANTIMONY AND BISMUTH IN COPPER ELECTROLYTES 4
2.2 SOLVENT EXTRACTION 9
2.2.1 Arsenic Extraction 11
2.2.1.1 Solvating Extractants 12
2.2.1.2 Acid Extractants 23
2.2.1.3 Basic Extractants 24
2.2.1.4 Chelating Extractants 24
2.2.2 Antimony Extraction 25
2.2.2.1 Solvating Extractants 25
2.2.2.2 Acid Extractants 25
2.2.2.3 Basic Extractants 25
2.2.2.4 Chelating Extractants 25
2.2.3 Bismuth Extraction 26
2.2.3.1 Solvating Extractants 26
2.2.3.2 Acid Extractants 26
2.2.3.3 Basic Extractants 26
2.2.3.4 Chelating Extractants 26
2.3 ION EXCHANGE 27
2.3.1 Introduction 27
2.3.2 Chemistry of Ion Exchange 27
2.3.2.1 The Resin Matrix 27
2.3.2.2 Functional Groups 28
2.3.3 Arsenic Extraction 31
2.3.3.1 Strong and Weak Acid Ion Exchangers 31
2.3.3.2 Strong and Weak Base Ion Exchangers 32
2.3.3.3 Chelating Ion Exchangers 32
2.3.3.4 Other Ion Exchangers 32
2.3.4 Antimony Extraction 33
2.3.4.1 Strong and Weak Acid Ion Exchangers 33
2.3.4.2 Strong and Weak Base Ion Exchangers 33
2.3.4.3 Chelating Ion Exchangers 34
2.3.4.4 Other Ion Exchangers 38
2.3.5 Bismuth Extraction 40
2.3.5.1 Strong and Weak Acid Ion Exchangers 40
2.3.5.2 Strong and Weak Base Ion Exchangers 40
2.3.5.3 Chelating Ion Exchangers 41
2.3.5.4 Other Ion Exchangers 41

3 SOLVENT EXTRACTION SCREENING EXPERIMENTS 42
3.1 INTRODUCTION 42
3.2 EXPERIMENTAL METHODS 42
3.3 ANALYTICAL TECHNIQUES 42
3.4 SHAKEOUT EXPERIMENTS 43
3.4.1 Results 44
3.5 MCCABE THIELE DISTRIBUTION ISOTHERMS 51
3.5.1 Arsenic Extraction 52

3.5.2 Antimony Extraction 56
3.5.3 Bismuth Extraction 57
3.5.4 Conclusions 58
3.6 STRIPPING STUDIES 58

4 ION EXCHANGE SCREENING EXPERIMENTS 67
4.1 EXPERIMENTAL METHODS 67
4.2 ANALYTICAL TECHNIQUES 68
4.3 SHAKEFLASK EXPERIMENTS 68
4.3.1 Results 69
4.4 COLUMN LOADING EXPERIMENTS 71
4.4.1 Arsenic Extraction 71
4.4.2 Antimony Extraction 72
4.4.3 Bismuth Extraction 75
4.5 COLUMN ELUTION EXPERIMENTS 78
4.5.1 Arsenic Elution 78
4.5.2 Antimony Elution 79
4.5.3 Bismuth Elution 81

5 SUMMARY AND CONCLUSIONS 85

6 REFERENCES 87

1 INTRODUCTION

The electrorefining of copper involves the anodic dissolution of an impure copper anode and the cathodic plating of a final copper product. Impurities in the anode either remain undissolved in an anode "slime" that forms on the surface of the electrode or anodically dissolve into the copper electrolyte. Silver and gold are examples of noble impurities which remain substantially undissolved in the anode slime during electrolysis. In contrast, a significant amount of arsenic, antimony, bismuth and nickel dissolve into the electrolyte during electrolysis. Impurities are incorporated into the cathode deposit by at least four mechanisms. First, some of the anode slime may "fall" from the anode and by convective transport arrive at the cathode surface and be incorporated. Second, precipitates of dissolved impurities (eg. $SbAsO_4$) may form in the bulk electrolyte and be incorporated into the cathode deposit. Third, electrolyte containing impurities may be trapped in micro spaces between copper crystals on the cathode surface. Fourth, impurities may codeposit with copper and contaminate the product. With respect to the second and third mechanisms, it follows that cathode purity may be maintained by ensuring that the concentrations of impurities in the bulk electrolyte are kept at low levels.

The purification of electrolyte is a tedious and expensive process. In a conventional purification scheme copper electrolyte is bled from the tankhouse circuit and sent to liberator cells. The copper is depleted from solution in the liberator (electrowinning) cells followed by depletion of arsenic, antimony and bismuth as a mixed cathode sludge. Following liberator cell treatment, the spent acid is evaporated, producing a concentrated waste acid and a nickel sulphate crystalline by-product. Figure 1.1 illustrates the conventional purification process, as practised at the Canadian Copper Refinery (CCR) in Montreal East (Thiriar, 1990).

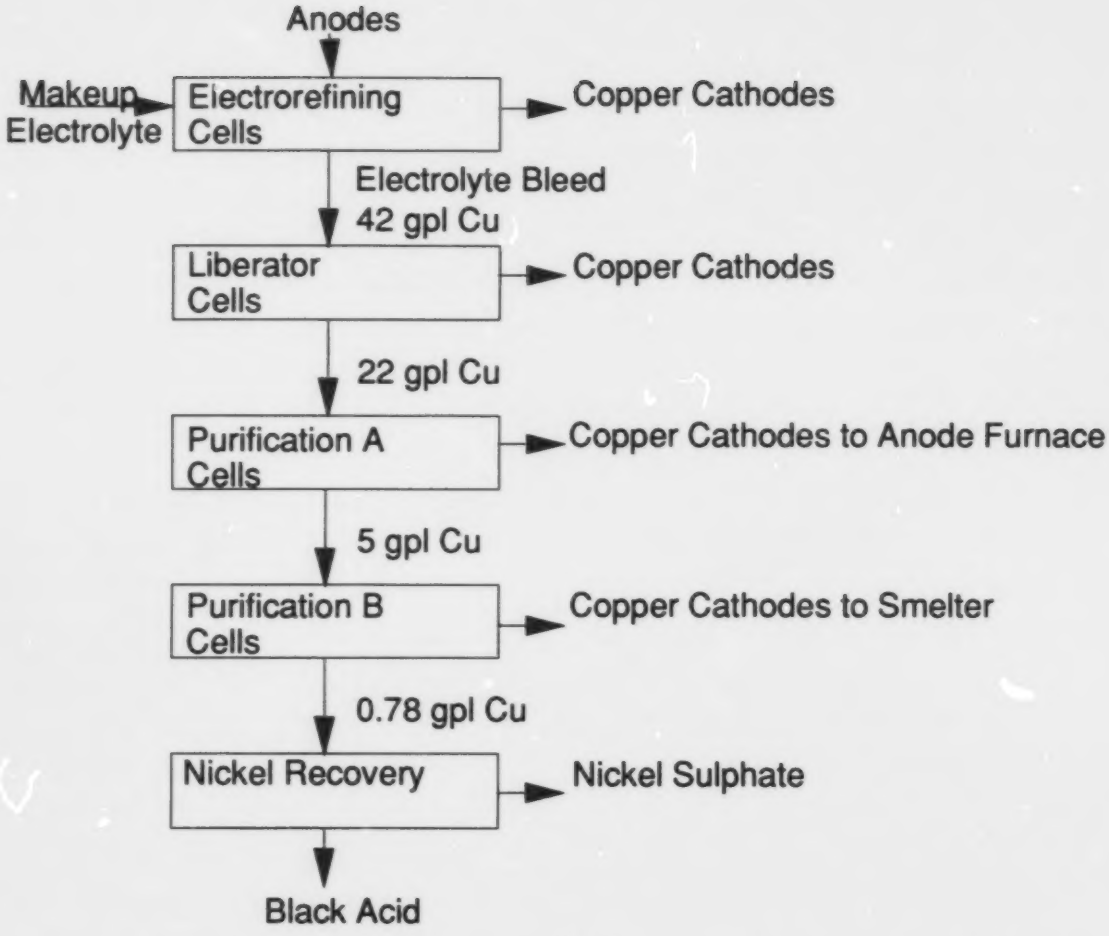

Figure 1.1. Conventional Flowsheet for Purification of Copper Refining Electrolyte (Thiriar, 1990)

The recent advances in solvent extraction and ion exchange chemistry and technology have allowed some changes in the conventional purification scheme. For example, arsenic is removed from copper electrolyte with TBP at MIM's Townsville copper refinery and recovered as a bicupric arsenate by-product (Hall et al., 1985 and O'Kane et al., 1985). The Tamano refinery at Okayama, Japan has developed a new process for antimony and bismuth removal (Shibata et al. 1987). Antimony and bismuth are adsorbed by a chelating resin designated UR-3300. The selectivity of the resin is Sb^{3+}, Bi^{3+}, Sb^{5+}, $Fe^{3+} > Mo^{6+} > Cu^{2+} > Fe^{2+} > Mn^{2+} > Ni^{2+}$. Antimony and bismuth are stripped quantitatively with HCl for the by-product recovery of antimony and bismuth chloride. At Sumitomo's Niihama Copper Refinery a process has been developed where antimony is removed from the electrolyte by contact with activated carbon (Toyabe et al., 1987).

Alternate reagents for impurity removal from copper electrolyte are also being investigated. For example, Rickleton and Brown (1985) have proposed that the reagent Cyanex 923 (a mixture of phosphine oxides) be used for arsenic, antimony and bismuth extraction from copper electrolyte. The main problem with Cyanex 923 appears to be that sulphuric acid is co-extracted with the impurities. A dilute sulphuric acid scrub liquor is produced in the proposed circuit which would have a negative impact on the plant water balance.

Clearly, there are distinct advantages to using solvent extraction and/or ion exchange techniques to remove arsenic, antimony and bismuth from solution rather than employing the conventional purification process.

1. There is no need to carry out the expensive electrowinning operation. Some evaporative treatment will still be required to remove nickel sulphate.
2. There is no copper-arsenic-bismuth-antimony electrolytic sludge requiring further processing.
3. There is no danger of producing arsine gas in liberator cells.
4. It may be possible to produce valuable by-products such as bicupric arsenate or antimony and bismuth chloride from solvent extraction and ion exchange processes.

There were two primary objectives in this study. The first objective was to survey the scientific and technical literature and determine what is known about the solvent extraction or ion exchange removal of arsenic, antimony and bismuth from acid electrolytes. This survey was supplemented by direct contact with reagent suppliers. The second objective was to perform laboratory scale research on reagents identified as the most promising in the literature search. Each reagent will be evaluated for the potential extraction of arsenic, antimony and bismuth.

2 INFORMATION SURVEY

A number of information sources was accessed to provide background to the experimental studies. First, a literature search on arsenic, antimony and bismuth solvent extraction and ion exchange was performed using the Chemical Abstracts System (STN). This search uncovered a large number of publications (technical papers, patents, etc.) for further examination. Second, various companies that produce solvent extraction extractants and ion exchange resins were contacted. The companies were asked to provide chemical samples of reagents that could be tested in this study. Third, copper refinery technical personnel were contacted via the "Copper Refining Group" (Canmet Secretariat). This group became the source of background information on purification problems in copper electrorefining.

The following subsections summarize the information gained from these sources. This body of knowledge provides a background for the experimental study which follows.

2.1 THE CHEMISTRY OF ARSENIC, ANTIMONY AND BISMUTH IN COPPER ELECTROLYTES

The aqueous chemistry of arsenic, antimony and bismuth is reasonably well documented. Figures 2.1-2.3 summarize the chemistry of the As-H_2O, Sb-H_2O and Bi-H_2O systems in the E_h - pH diagram format. All diagrams were drawn using the CSIRO Thermochemistry program for a temperature of 25°C. The E_h - pH diagram format is limited by the availability of thermodynamic data. Other species may exist, but have not been included because of the lack of published free energy data.

Cotton and Wilkinson (1988) have provided a brief summary of the chemistry of arsenic, antimony and bismuth which complements the information in the E_h - pH diagrams. They report that in sulphuric acid from 0.5 to 12 M, pentavalent antimony seems to be present as $Sb_3O_9^{3-}$. For trivalent antimony, the species depends on the acid concentration. From 0 to 1.5 M sulphuric acid the dominant species is SbO^+ or $Sb(OH)_2^+$. From ~1 to 18 M sulphuric, the species $SbOSO_4^-$ and $Sb(SO_4)_2^-$ appeared. In the case of bismuth, Cotton and Wilkinson state that there is no evidence for a simple bismuth aqua ion $[Bi(H_2O)_n]^{3+}$. They report that in neutral perchlorate solutions the main species is $Bi_6O_6^{6+}$ or its hydrated form $Bi_6(OH)_{12}^{6+}$. No information on bismuth ion - sulphate interactions is given.

Copper refining electrolytes are chemically more complex than simple binary mixtures. These electrolytes contain major amounts of sulphuric acid (150-200 g/L), copper sulphate and nickel sulphate and minor amounts of a number of other species. In addition, electrorefining is carried out at elevated temperature (~60°C) in the presence of organic additives. These organic additives may also interact with the impurities.

Nevertheless, the E_h - pH diagrams can be used to postulate which arsenic, antimony and bismuth species exist in these electrolytes. Arsenic(V) is the predominate form of arsenic in copper electrolytes. Figure 2.1 indicates that at pH values close to 0, the neutral species H_3AsO_4 dominates. Minor amounts (probably less than 10%) of arsenic(III) are also present in copper electrolyte. The dominant form for arsenic(III) is the neutral species $HAsO_2$[1]. This information suggests that a solvent extractant or an ion exchanger that is selective for neutral species may be useful for extracting arsenic[2].

The trivalent forms of antimony predominate in copper electrolyte[3]. From Figure 2.2, at pH values just below 0, the cationic species SbO^+ dominates. At pH values greater than 0, the solid species Sb_2O_3 appears. It may well be that a neutral species such as $HSbO_2$ could exist in this area of the predominance diagram. If the activity of solute species decreased (set at 0.0001 in Figure 2.2), this species would appear in place of Sb_2O_3. If any antimony exists in solution in the pentavalent oxidation state, it could either exist as the cation SbO_2^+ (pH values below 0) or the anion SbO_3^- (pH values above 0). It may therefore be concluded that an extractant or ion exchanger that extracts cations or neutral species may be useful for extracting antimony(III) from copper refining electrolytes. If any antimony(V) is present, the extracting reagent would have to be able to extract cationic or anionic species.

The trivalent form of bismuth is certain to dominate in copper refining electrolytes. Figure 2.3 predicts an ionic species Bi^{3+} over a wide potential and pH region. It is therefore predicted that a cationic extractant or ion exchanger would have the best chance of extracting bismuth from copper electrolytes.

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1 The species $HAsO_2$ is equivalent to the oft cited species H_3AsO_3. Both species are referred to as arsenious acid.

2 This statement is partly based on hindsight. It is well known that the solvating extractant tri-butyl-phosphate extracts both neutral arsenic acid species.

3 It is widely believed that the presence of a small amount of arsenic(III) is beneficial in copper refining. Arsenic(III) probably suppresses the formation of antimony(V) by buffering the redox potential of the solution. Antimony(V) often forms insoluble precipitates (Abe et al., 1987).

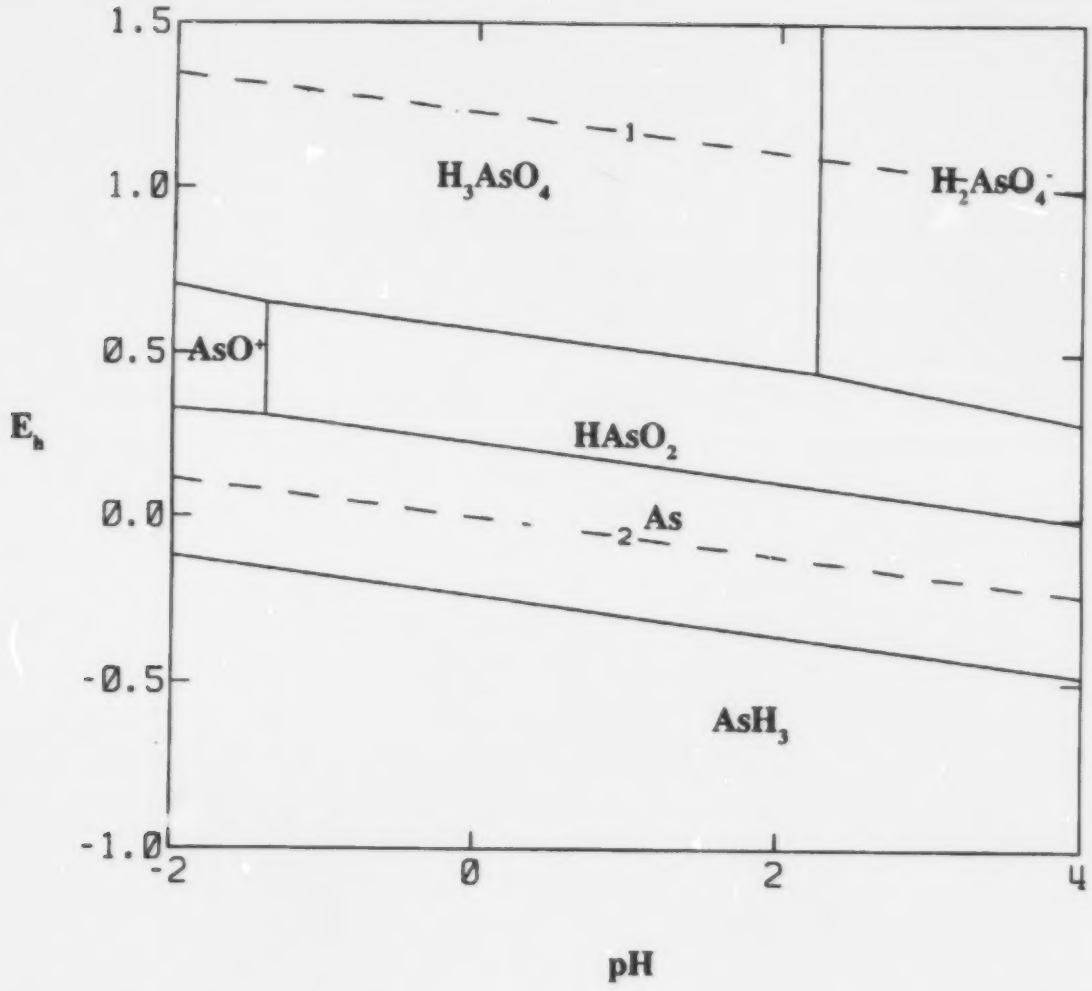


Figure 2.1 Eh - pH diagram for the As-H_2O system. Solute activities of 0.1. Gas species activities of 1.

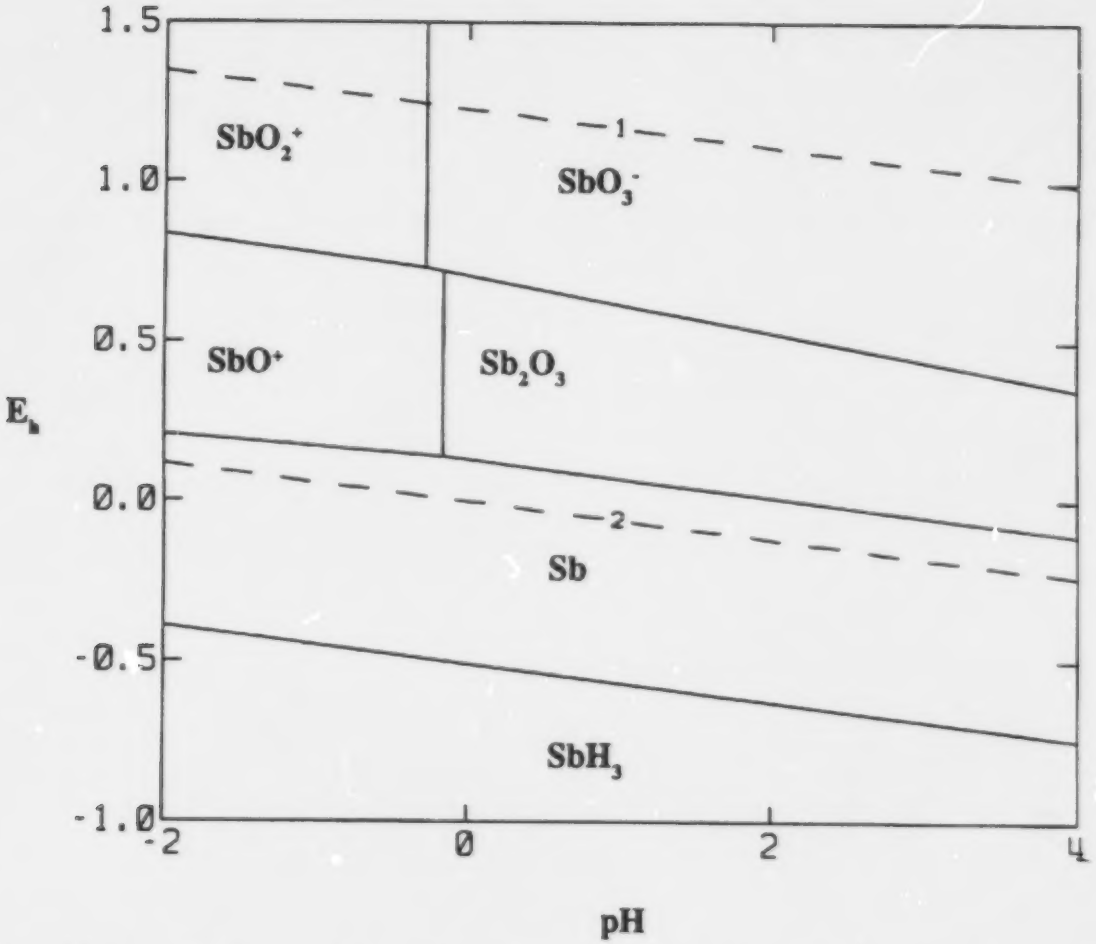


Figure 2.2 Eh - pH diagram for the Sb-H_2O system. Solute activities of 0.0001. Gas species activities of 1.

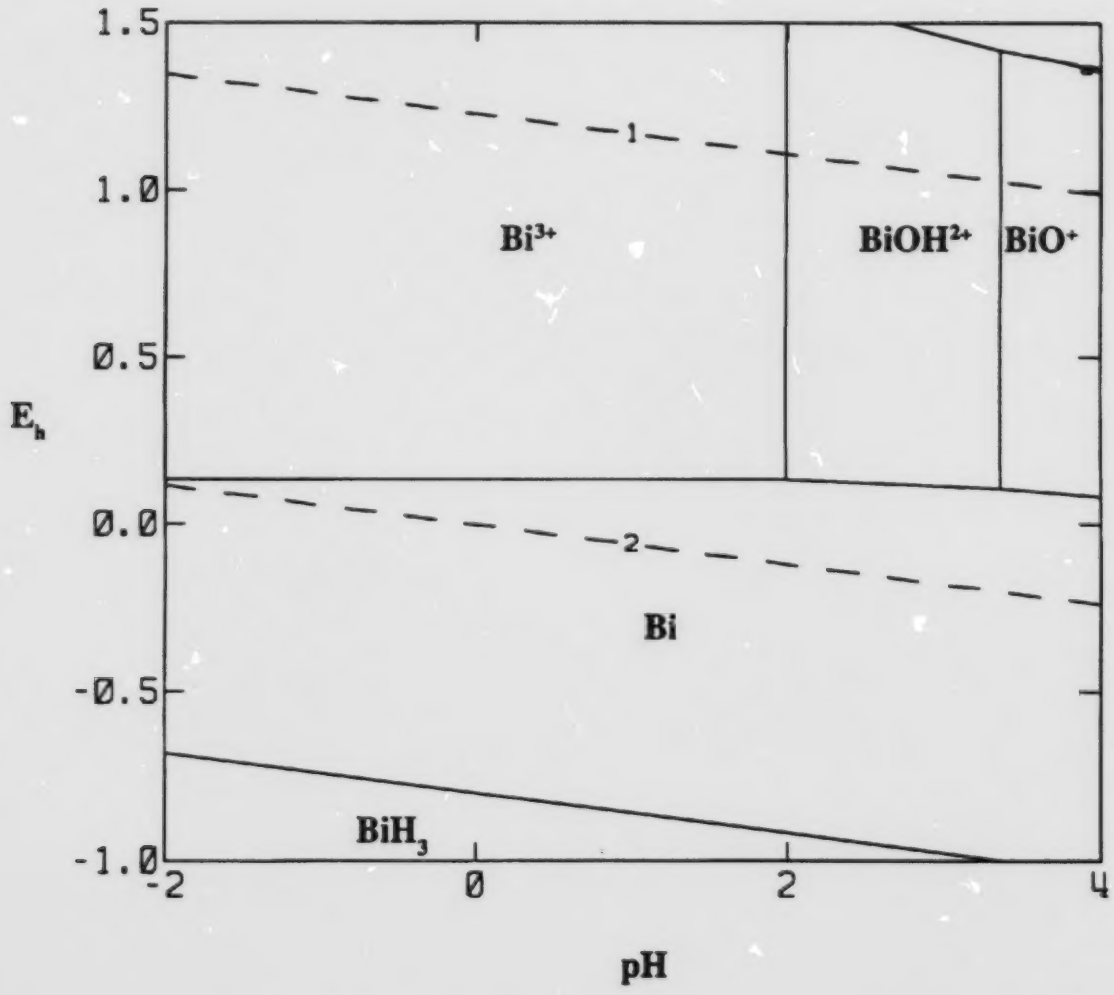


Figure 2.3 Eh - pH diagram for the Bi-H_2O system. Solute activities of 0.0001. Gas species activities of 1.

Nishimura and Tozawa (1986) reported on the solubilities of arsenic and antimony in water and water - sulphuric acid solutions. These authors noted a wide number of antimony sulphate and arsenic sulphate precipitates. When both metals were present together with sulphuric acid, the precipitate species $SbAsO_4$ was detected.

Abe and Takasawa (1987) studied the formation of floating slimes in copper electrolytes. Figure 2.4 illustrates some of their results. It is apparent that significant interaction between the arsenic, antimony and bismuth species takes place in copper electrolytes. Plant electrolytes and synthetic electrolytes behaved differently. Additive effects were also significant.

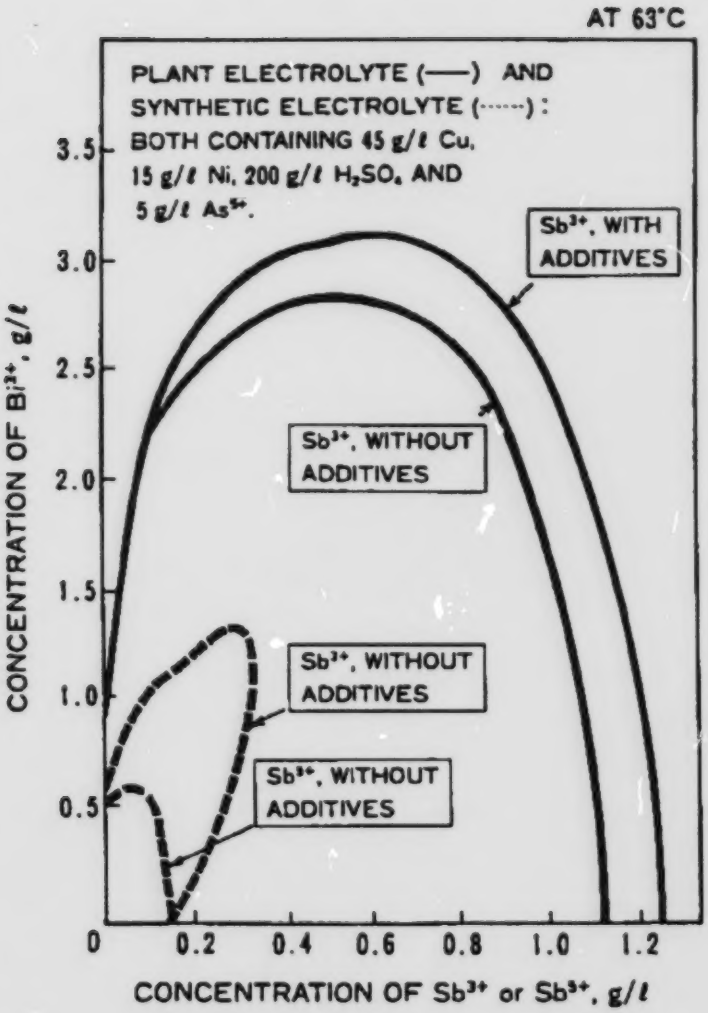


Figure 2.4. Solubility Diagram of the As-Sb-Bi Ternary System Showing the Effect of Sb Ions. (after Abe and Takasawa, 1987).

2.2 SOLVENT EXTRACTION

The chemistry of solvent extraction is most clearly understood when the components of the organic solution are considered independently. The components to be considered are the extractant, the diluent, the accelerator and the modifier. The extractant is the species that forms an organic soluble complex with the metal ion. The diluent is an organic solvent that is used to dilute the

extractant concentration to the appropriate level for metal extraction and stripping. An accelerator is added when the kinetics are too slow. A modifier is used to improve the chemical or physical performance (settling behaviour) of the solvent extraction system.

Hudson (1982) has listed a number of general features of an extractant employed in the commercial separation of metals. Unfortunately, it is unlikely that any one extractant can meet these sometimes conflicting criteria. However, in general a balance among the criteria is sought.

1. The ability to extract the metal at the required pH.
2. To be selective for the required metal and to reject undesired metals.
3. To have acceptable rates of extraction, scrubbing and stripping.
4. To be soluble in the organic phase and to have a limited solubility in the aqueous phase.
5. To be stable throughout the three principal stages of solvent extraction (extraction, scrubbing and stripping).

Extractants for the solvent extraction of metals have been conveniently grouped into four categories: acid extractants, acid chelating extractants, basic extractants and solvating extractants. Table 2.1 shows a summary of the types of extractants available.

In the following subsections the solvent extraction behaviour of arsenic, antimony and bismuth will be surveyed. Where possible, commercial applications have been cited.

Table 2.1. Solvent Extraction Reagents for Hydrometallurgy (Flett et al., 1983 and Flett and Spink, 1976).

Class	Type	Examples	Manufacturers	Commercial Uses
Acid extractants	Carboxylic acids	Naphthenic acids	Shell Chemical Co.	Copper–nickel separation
	Alkyl phosphoric acids	Di-2-ethylhexylphosphoric acid (D2EHPA)	Union Carbide	Yttrium recovery, europium extraction, nickel–cobalt separation
		Octylphenylphosphoric acid (OPPA)	Mobil Oil Co.	Uranium extraction
	Aryl sulfonic acids	SYNEX 1051	King Industries, Inc.	Magnesium extraction
Acid chelating extractants	Hydroxyoximes	LIX63, LIX64N, LIX65N, LIX70	Henkel Corporation	Copper and nickel extraction
		SME 529	Shell Chemical Co.	Copper extraction
		P5000 series	Acorga Ltd.	Copper extraction
	Oxine derivatives	Kelex 100	Sherex Chemical Co.[a]	Proposed for copper extraction
	β-Diketones	Hostarex DK16	Farbwerke Hoechst AG	Proposed for copper extraction from ammoniacal solution
		LIX54	Henkel Corporation	Copper extraction from ammoniacal extraction
		XI51	Henkel Corporation	Proposed for cobalt extraction from ammoniacal solution
	Alkarylsulfonamide	LIX34	Henkel Corporation	Proposed for copper extraction from acidic leach liquors
	Polyols		Dow Chemical Co.	Boron extraction
Anion exchangers	Primary amines	Primene JMT	Rohm and Haas	No known commercial use
	Secondary amines	LA-2	Rohm and Haas	Zinc and uranium extraction
		Adogen 283	Sherex Chemical Co.[a]	Zinc and tungsten extraction
	Tertiary amines	Various Alamines; in particular Alamine 336	Henkel Corporation	Widely used; cobalt, tungsten, vanadium, uranium extractions etc.
		Various Adogens; in particular Adogen 364, Adogen 381, Adogen 382	Sherex Chemical Co.[a]	Cobalt, vanadium, and uranium extractions
	Quaternary amines	Aliquat 336	Henkel Corporation	Vanadium extraction; other possible uses are chromium, tungsten, and uranium extraction
		Adogen 464	Sherex Chemical Co.[a]	Similar to Aliquat 336
Solvating extractants	Phosphoric, phosphonic, and phosphinic acid esters	Tributyl phosphate (TBP)	Union Carbide, Albright and Wilson	Nuclear fuel reprocessing, U_3O_8 refining, iron extraction, zirconium–hafnium separation, niobium–tantalum separation, rare earth separations, acid extraction
		Phosphonic acid esters	Farbwerke Hoechst AG	No known commercial use
		Trioctylphosphine oxide (TOPO)	Henkel Corporation Cyanamid	Recovery of uranium from wet process phosphoric acid liquors (with D2EHPA)
	Various alcohols, ethers, ketones	Butanol–pentanol	Various	Phosphoric acid extraction
		Diisopropyl ether	Various	Phosphoric acid extraction
		Methyl isobutyl ketone (MIBK)	Various	Niobium-tantalum separation, zirconium-hafnium separation
	Alkyl sulfides	Di-n-hexyl sulfide		Palladium extraction

[a]Previously Ashland Chemical Co.

2.2.1 Arsenic Extraction

The solvent extraction of arsenic has been widely reported. The following subsections summarize the literature on arsenic extraction from acidic solutions.

2.2.1.1 Solvating Extractants

Solvating extractants extract neutral species from the aqueous solution. Analysis of the solution chemistry of arsenic indicated that the neutral species H_3AsO_4 and $HAsO_2$ would be formed in acidic sulphate solutions. It is therefore likely that solvating extractants would be useful for arsenic extraction.

The most commonly employed solvating extractant is tri-butyl-phosphate (TBP). There are a number of reports of arsenic extraction with TBP.

One of the earliest references to arsenic extraction with TBP was by Tserekova et al. (1970, 1972). This early work has been developed into a number of patents and commercial processes using TBP.

MHO SX As Process

De Schepper (1977, 1978 and 1985) reports the extraction of arsenic from a concentrated electrolyte bleed-stream using undiluted TBP at Metallurgie Hoboken-Overpelt (MHO) in Belgium. A process was developed to extract arsenic from the Olen copper tankhouse bleed. The positioning of this process within the Olen refinery is shown in Figure 2.5. Under this method the most important parameters examined were the effects of acidity, organic concentration and temperature on the overall impurity removal. These factors are reviewed in turn in the following sections.

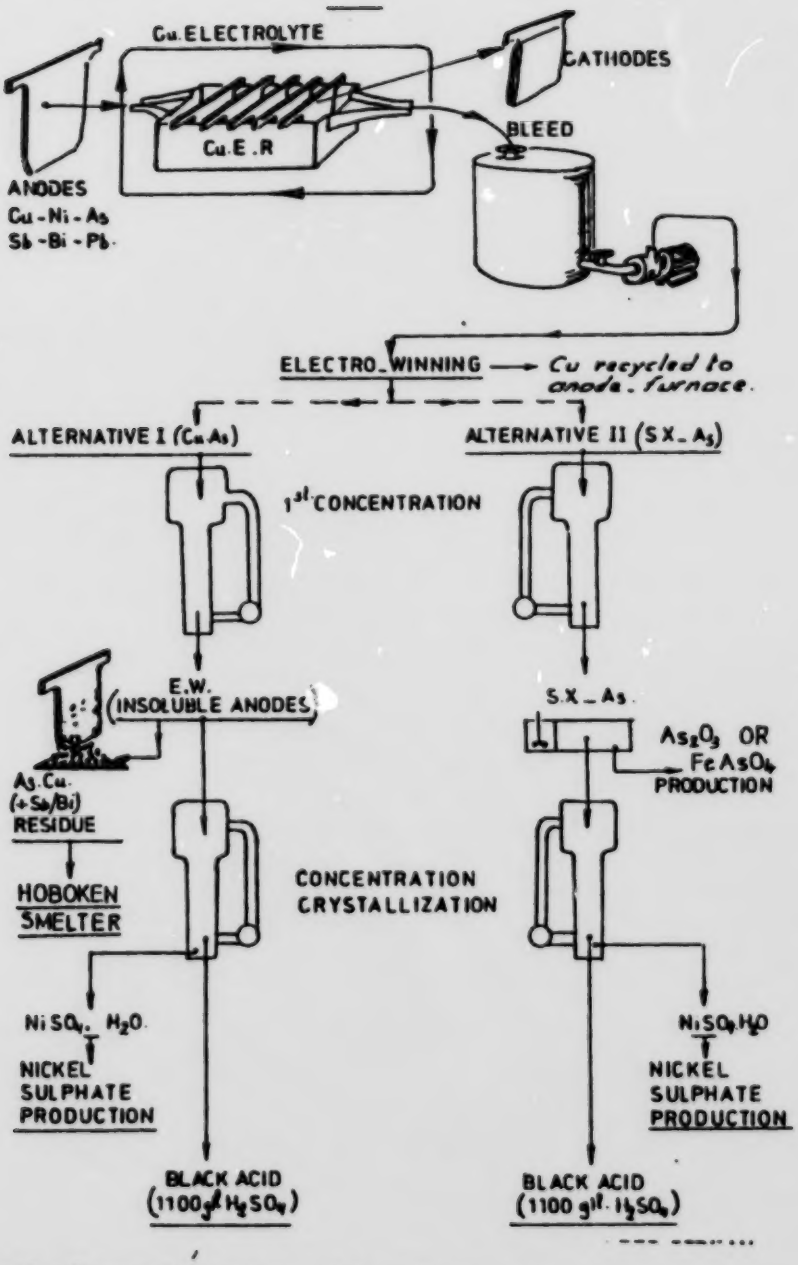


Fig. 2.5. Alternative Routes for As Removal from Cu-Bleed Stream. Alt. I: "Classical System", Alt. II: "The MHO SX As Process" (De Schepper, 1985).

In Figure 2.6 it appears that the distribution coefficient, $K_D(As)$, is highly dependent on the free sulphuric acid content of the electrolyte. It can be seen that the concentration of free H_2SO_4 must exceed 250 g/L to achieve a relatively high distribution coefficient of arsenic. As a result, the

MHO solvent extraction process was designed to operate at high acid concentrations to take advantage of the large distribution coefficient for arsenic. Also, this would allow a smaller volume of aqueous phase to be treated. It was stated that TBP remains fairly stable at acid concentrations of 550 g H_2SO_4/L, but it will degrade upon use at elevated temperatures at acid concentrations in the range of 1100 g/L.

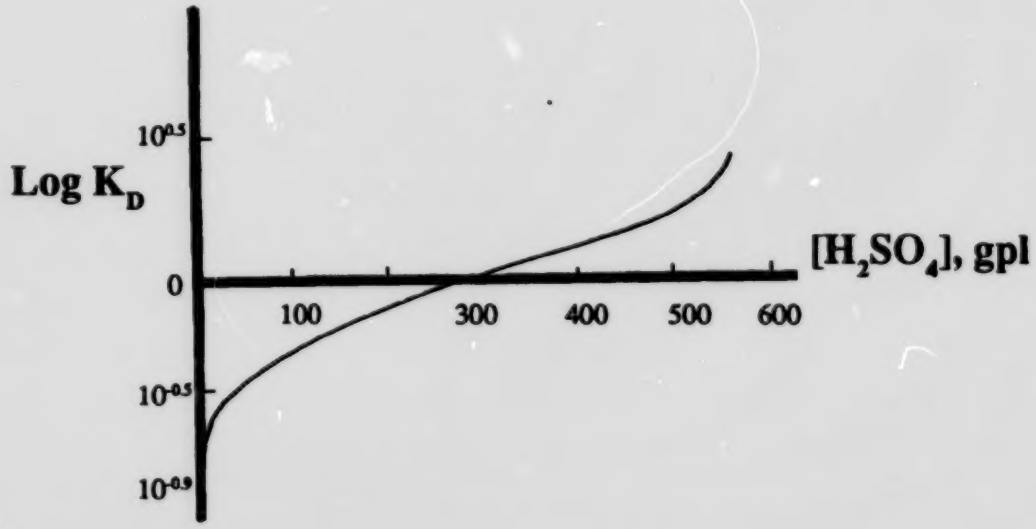


Figure 2.6. Relationship between Log K_D and the Free Sulphuric Acid Content in the Aqueous Phase at Equilibrium with Undiluted TBP at 25°C (De Schepper, 1985).

As expected, the concentration of TBP in the organic phase greatly affects its loading capacity. A "third-phase" was less likely to form when undiluted TBP was employed and the maximum solubility of arsenic in the organic phase was reached, otherwise modifiers such as isodecanol had to be added. As well, the use of diluents is not particularly amenable to the operating temperatures necessary for electrolysis in copper refining. Because the flash point of most diluents suitable for this application is near 70°C, the organic mixtures may constitute a hazard when they contact electrolyte streams in the temperature range of 50 - 65°C.

The distribution coefficient of As is also influenced by the electrolyte temperature. At an O/A ratio = 1, tests revealed that an increase in the temperature of the bleed-stream from 20°C to 50°C lead to a 5% decrease in the overall extraction yield, although the extraction yield itself remained linearly dependent on the concentration of TBP. By operating at a higher O/A ratio, this decrease in extraction could be offset.

The process flowsheet is shown in Figure 2.7. The pregnant strip solution can be treated for recovery of arsenic trioxide or ferric arsenate.

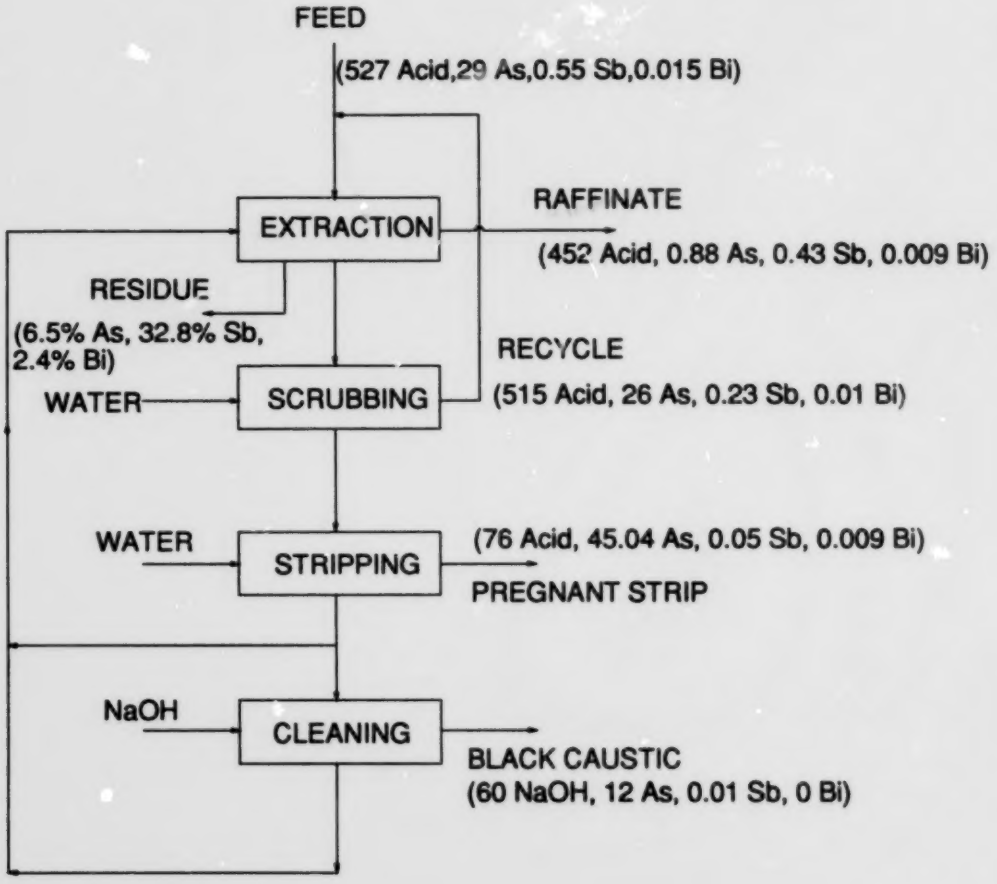


Figure 2.7. Basic Pilot Plant Flowsheet - MHO Process for Arsenic Removal using TBP (De Schepper, 1985). Values in g/L except where otherwise noted.

The formation of a solid material in the extraction mixer-settler caused problems with the original pilot plant design. However, these problems were overcome by the design of a novel mixer-settler with the unique ability to handle small amounts of precipitated solids. This mixer design is outlined by De Schepper (1981, 1983).

The MHO process has apparently performed very well for a period in excess of 10 years. The advantages of this process are:

1. Economically attractive.
2. Avoidance of arsine generation.
3. Stable extractant.
4. Arsenic recovered as a by-product (As_2O_3) or a stable residue ($FeAsO_4.2H_2O$).

The disadvantages of the process are:

1. TBP is slightly soluble in the copper electrolyte and it adversely affects the electrolysis of copper.
2. Antimony and bismuth are not extracted to the same extent as arsenic.
3. Acid is co-extracted.
4. Organic additives are solvated by TBP. These additives have to be stripped from the TBP by the caustic wash.
5. The precipitation of a solid phase in extraction is undesirable.
6. The precipitation of ferric arsenate is undesirable. The disposal of this waste material incurs extra expense for the process.

MIM SX As Process

The MIM process has been described in numerous publications (Royston, 1982, Royston et al., 1984, Hall et al., 1985, O'Kane, 1985). The process is referred to as the BiCupric Arsenate (BCA) Process. Arsenic is selectively extracted from the copper electrolyte with TBP in a kerosene diluent. After stripping with water, the arsenic is precipitated as bicupric arsenate, a product which is sold to the wood preservative industry. Hall et al. (1985) describe the complete development and optimization of the process from bench-scale tests using mixer-settlers to a commercial plant. The process itself has replaced the conventional electrodeposition method and is designed particularly for Townsville copper electrorefining practices. It is the goal of this process to remove arsenic selectively over copper, antimony and bismuth in order to produce bicupric arsenate (BCA).

Typical compositions of the electrolyte liquors used in the Townsville investigations can be seen in Table 2.2. The copper tank house electrolyte is maintained at 62°C and contains 40-55 g/L Cu and 180 g/L H_2SO_4. Also, a number of kerosene diluents were examined, namely Shellsol T (an aliphatic hydrocarbon), Shellsol A (an aromatic hydrocarbon) and Shellsol 2046 (an aliphatic/aromatic hydrocarbon). Initial studies indicated that high acid conditions facilitated

arsenic loading in the solvent. This result is consistent with the MHO development. Furthermore, arsenic could be removed from the organic phase with water, resulting in a strip liquor relatively low in acid concentration.

Table 2.2. Electrolyte Liquor Compositions (g/L) Used in Experiments at MIM.

	H_2SO_4	Cu^{2+}	As^{5+}	Ni^{2+}	Sb^{3+}	Bi^{3+}
Tank House Electrolyte	170 - 200	44-55	15-18	18-19	0.06	0.04
Liberator Electrolyte	175 - 250	28-30	15-18	18-19	0.06	0.04

The flowsheet shown in Figure 2.8 details the basic plant design developed from work conducted using pilot plant mixer-settlers. Tests helped to determine the optimum organic/aqueous ratios and TBP/kerosene ratios (50% TBP in Shellsol 2046). Aqueous to organic ratios of 1:6 (Extraction), 1:80 (Scrubbing) and 1:12 (Stripping) were employed in the plant design. Bicupric arsenate is produced from solvent extraction strip liquor and copper sulphate solution. Either NaOH or NH_3 may be used as neutralizing agents in the BCA process.

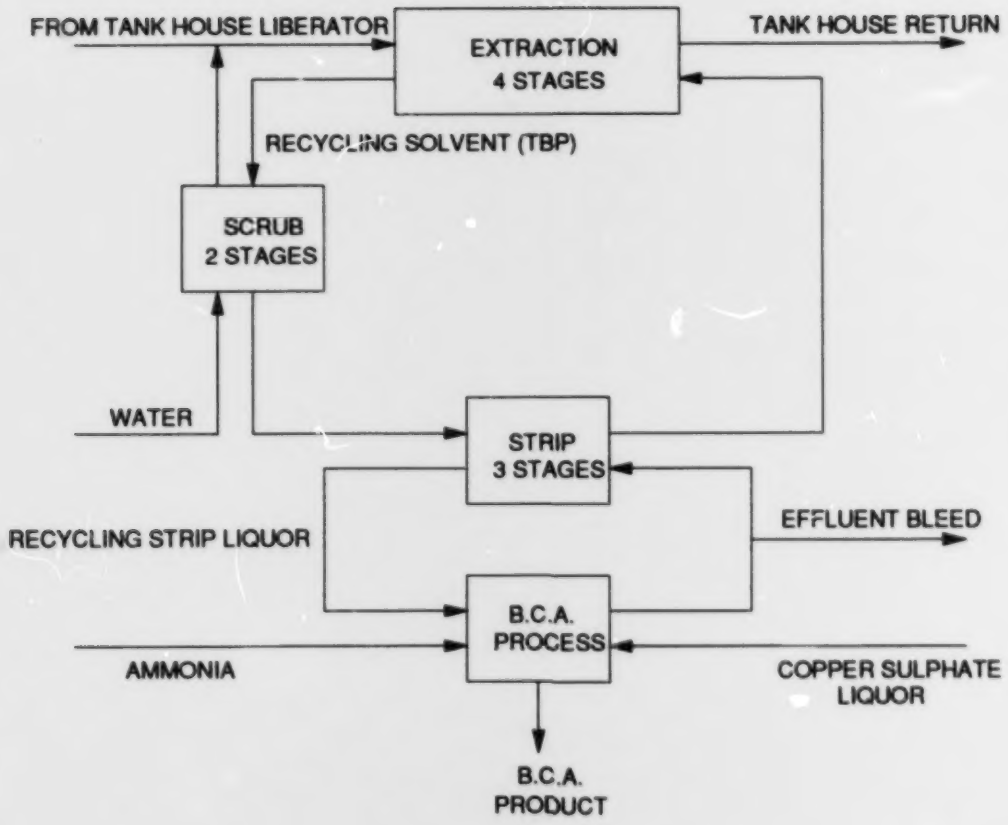


Figure 2.8. The Solvent Extraction Bicupric Arsenate Process (Hall et al., 1985).

The advantages of the solvent extraction process are:

1. No risk of arsine formation.
2. Removal of copper, to control copper concentration in the tankhouse, can be carried out separately from arsenic removal. This results in higher quality electrowon copper and a substantial decrease in the return of poor quality cathode for reprocessing by smelting or melting.
3. Lower power consumption.
4. Cheaper costs in production and better marketability of the pentavalent arsenic product, as opposed to trivalent arsenic, for use in wood preservatives.

5. Materials handling of starting sheets and deposited materials is eliminated in the arsenic removal step.

6. The production, storage for oxidation, handling and processing of the copper arsenic sludge which results from conventional arsenic control is eliminated along with the associated hygiene and environmental factors.

7. Lower labour and maintenance costs.

The disadvantages of this process are:

1. Higher solvent inventory than the MHO process

2. Higher risk of fire due to the use of the solvent Shellsol 2046[4]

Other workers have also investigated the extraction of arsenic with TBP. The following paragraphs summarize this work.

Kerfoot (1978) studied and patented a solvent extraction process for the elimination of arsenic from copper/nickel-bearing acidic media. Solutions containing from 100 - 600 g/L sulphuric acid could be effectively purified with a mixture of 40-75 vol.% TBP, 15 vol.% quaternary ammonium reagent and an organic diluent. Examples of some of these commercial chemicals are listed in Table 2.3.

Table 2.3. Some Diluents and Chemical Modifiers for Use with TBP.

Diluents	Quaternary Ammonium Reagents
Kerosene Escaid 100 Isopar K Varsol DX3641 Shell 140 Shell-Sol 715	Aliquat 336 (tricaprylmethyl-ammonium chloride) Adogen 464 (tri-C8-C10 methylammonium chloride)

4 Shellsol 2046 has a flashpoint of 80°C. This is relatively high for a solvent. However, an operating temperature of over 60°C in the solvent extraction circuit is relatively close to the flash point. Hence the greater risk of fire. Note that the flashpoint for undiluted TBP is 152°C.

It was found from a number of batch shake-out tests conducted at 25°C that a mixture of 60 vol.% TBP and 5 vol.% Aliquat 336 in Escaid 100 could extract 61.2% of the As in two contacts. The composition of the electrolyte used in the testwork is given in Table 2.4. Copper and nickel did not coextract. At acid concentrations of 300 - 600 g/L H_2SO_4, the addition of quaternary ammonium reagents to the organic phase did not result in any change in extraction behaviour for arsenic.

Table 2.4. Composition of the Electrolyte used in Kerfoot's Work.

H_2SO_4	Cu	As	Sb	Bi
304 g/L	27.0 g/L	3.02 g/L	0.22 g/L	56.8 mg/l

Kerfoot suggested several options for stripping the loaded organic which included water, sodium carbonate, NaOH, and H_2SO_4. The most effective agents were dilute NaOH or dilute H_2SO_4. When water was used, phase disengagement was very slow. For all other stripping agents, phase disengagement was also slow but acceptable.

For arsenic removal from solutions containing arsenic and copper, Takahashi et al. (1978) investigated the extraction behaviour of an organic phase consisting of 50-75% TBP and 2-ethyl hexanol or dodecyl alcohol. Their patent suggested stripping the loaded organic phase with a neutral or alkaline aqueous solution (NaOH, Na_2CO_3, etc.). Arsenic extractions of over 90% were achieved in multiple contact experiments. Arsenic was easily stripped to very low levels in the organic.

Demirkiran (1978) reported on the design of a solvent extraction circuit for arsenic removal using tri-butyl-phosphate. This work is heavily referenced in the development of the MIM process reviewed in an earlier section.

Nagai (1985) and Nagai et al. (1985) have reported the use of TBP for the removal of impurities in copper sulphate - sulphuric acid solutions. Nagai and his co-authors have approached this in a number of ways and their techniques are examined below.

Nagai et al. (1985) investigated the removal of arsenic from spent copper electrolyte using tri-butyl-phosphate (TBP) in a series of batch-wise, step-wise and continuous counter-current extraction tests. The optimum conditions for extraction were at temperatures of 55°C with undiluted TBP at an O/A ratio of 2, followed by stripping at an O/A ratio of 5. It was noted that these conditions

were comparable to those commonly used for mother liquors in operating plants, with the exception that O/A ratio should be less than 3 during stripping. More than 85% of the total arsenic could be removed from the mother liquor and the spent copper electrolyte.

Also in 1985, Nagai patented another treatment process utilizing TBP for the removal of arsenic in copper electrolytes. The following is a summary of the process results.

Chemistry:

Copper electrolyte:	4.91 g/L As 190 g/L H_2SO_4
Extraction:	TBP, 5 stages, O/A ratio = 2, temp. = 35°C
Scrubbing:	water, 2 stages, O/A ratio = 10, temp. = 45°C
Stripping:	2 stages, O/A ratio = 10, temp. = 45°C aqueous NH_4OH, $(NH_4)_2SO_4$ used as back extractant, yielding 10 g/L As

The stripping solution was treated with $Ca(OH)_2$ to regenerate NH_3 and precipitate calcium arsenate. Arsenic was releached with acid, reduced with SO_2 and precipitated as As_2O_3. The waste product gypsum contained 0.76% As.

$$2(NH_4)_3AsO_4 + 3Ca(OH)_2 = Ca_3(AsO_4)_2\ (s) + 6NH_3 + 6H_2O$$

$$(NH_4)_2SO_4 + Ca(OH)_2 = CaSO_4 \cdot 2H_2O\ (s) + 2NH_3$$

$$Ca_3(AsO_4)_2 + 3H_2SO_4 + 2H_2O = 2H_3AsO_4 + 3CaSO_4 \cdot 2H_2O\ (s)$$

$$2H_3AsO_4 + 2SO_2 = As_2O_3\ (s) + 2H_2SO_4 + H_2O$$

It is unclear how this process was patented. The chemistry of extraction, scrubbing and stripping are all contained in patents and publications of MHO and MIM. The treatment of the strip solution to precipitate arsenic and regenerate ammonia may be novel. However, this treatment does not seem to be advantageous. The end result is an arsenic-contaminated gypsum and a solid arsenic trioxide.

Navarro et al. (1981) have also reported an investigation of TBP extraction of arsenic from copper electrolytes. Results were similar to those reported by other groups.

Marr, Bart and Wachter (1983) reported the extraction of arsenic with tri-isooctyl phosphine oxide (TOPO). These authors claim that TOPO is a much stronger extractant for arsenic than TBP. Unfortunately, TOPO is a solid at room temperature and is not very soluble in organic solvents. It is therefore difficult to use in the present application.

Rickelton and Brown (1985) have investigated the removal of arsenic, antimony and bismuth from copper-nickel electrolytes by solvent extraction with liquid phosphine oxides. Cyanex 923 is a mixture of four trialkyl phosphine oxides and has an average molecular weight of approximately 350 g/mol. It can be used undiluted or alternately can be mixed with hydrocarbon diluents. It is a liquid at room temperature. It is more viscous than TBP, 40 cp at 25°C versus 6.0 cp at the same temperature for TBP. In the experiments reported by Rickelton and Brown, Cyanex 923 was a stronger extractant for arsenic than TBP. However, Cyanex 923 also extracted significant amounts of acid. For example, starting from an aqueous solution of 31.4 g/L Cu, 167.2 g/L H_2SO_4 and 8.0 g/L As, at an A/O ratio of 1, the acid concentration in Cyanex 923 was 51.3 g/L (31.0% extraction) whereas the concentration in TBP was 6.2 g/L (3.7% extraction). The coextraction of acid by Cyanex 923 results in a difficult scrubbing operation in a potential commercial circuit.

SAMIM researchers reported the use of long chain alcohols to extract arsenic from copper refining solutions (Guerriero et al., 1985, Baradel and Guerriero, 1986, Baradel et al., 1986, 1987, 1988). In the report by Baradel et al., 1986, the extraction of both trivalent and pentavalent arsenic by a number of long chain alcohols is noted. The reagent 2-ethyl-1-hexanol was selected as the extractant of choice. 2-ethyl-1-hexanol is a stronger extractant for trivalent arsenic than pentavalent arsenic. There were other alcohols that were better extractants for pentavalent arsenic than 2-ethyl-1-hexanol (eg. 1-pentanol). However, 1-pentanol is relatively soluble in water, coextracts a significant amount of water along with arsenic and has a low flash point. Each of these characteristics make it undesirable in the present application. Even 2-ethyl-1-hexanol is relatively water soluble (0.7 g/L) and also has a relatively low flashpoint (85°C). Apparently, it does not coextract sulphuric acid. Stripping of arsenic is carried out with water or sodium sulphate solutions or with caustic solutions.

Earlier work by Shkinev et al. (1978) revealed that As(V) could be effectively extracted using dinonyltin dinitrate. In this case, arsenic was removed from HNO_3, $HClO_4$ and H_2SO_4 solutions and extracted into $CHCl_3$ containing 30% BuOH. The abstract did not reveal the amount of extraction. Later, Shkinev et al. (1981) investigated the extraction behaviour of arsenic using dialkyltin dinitrates (DATDN) of the form:

$$R_2Sn(NO_3)_2$$

where R indicates an alkyl group. As(V) was selectively extracted from large volumes of aqueous solutions of metal salts and mineral acids. This procedure was developed particularly for determining As levels in steel, cast iron and copper.

2.2.1.2 Acid Extractants

A number of acid extractants have been reported for arsenic extraction. The following subsections summarize the behaviour of these reagents.

Hydroxamic Acids

The use of hydroxamic acid extractants to extract arsenic, antimony and bismuth has been described (Schwab and Kroke, 1988, Schwab and Buchmeier, 1988, Schwab and Kehl, 1989). As, Sb, Bi, and Fe are all extracted by these extractants. Unfortunately, they are so strongly extracted that it is difficult to strip them. In 1988, Schwab and Kroke reported a three-stage solvent extraction process using the extractant XI-104 (hydroxamic acid) to remove contaminants in copper electrolytes. The key steps are: 1) simultaneous extraction of As, Sb, Bi, and Fe using XI-104, 2) stripping of As, Sb and Bi by sulphide precipitation (H_2S) and 3) separate stripping and complexing of Fe with suitable H_2O-soluble agents.

The structure and formula of the extractant were reported in the patent by Schwab and Kehl (1989). The hydroxamic acid extractant is synthesized by reacting a Versatic acid extractant (tertiary mono carboxylic acid) with an excess of $SOCl_2$ to form the corresponding acid chloride followed by reaction with hydroxylamine. Alternately, the Versatic acid extractant can be converted to its alkyl ester followed by reaction with hydroxylamine. In both cases the reaction product is a hydroxamic acid reagent. The characteristics of XI-104 include 1) good solubility in kerosene, 2) stable extraction at high temperatures and high acid concentrations (preferably 150-250 g H_2SO_4/l), 3) no coextraction of free acid, 4) simultaneous extraction of all impurities effected without elevated acid concentrations, 5) no "third-phase" formation which would require the addition of modifiers to the organic phase and 6) no deleterious side effects to the overall solvent extraction process. However, XI-104 is unstable with increasing alkalinity and acidity (particularly at H_2SO_4 concentrations exceeding 400 g/L). It is also reported to be unstable with respect to oxidation.

The concentration of XI-104 in the organic phase for optimum extraction is mainly dependent on the concentration of As as the other major impurity. It is relatively easy to get quantitative extraction of antimony, bismuth and ferric iron. Arsenic extraction is more difficult. Improved extraction of arsenic and the other contaminants occurred with longer contacting times and slightly higher temperatures (60°C). Arsenic can be extracted as As(III) or As(V).

Conversion of all the impurity elements to their sulfides, with the exception of Fe, is made possible by contacting the loaded organic with either acidic H_2S gas or anhydrous sodium sulfide in an autoclave. H_2S is preferred because it helps to regenerate XI-104, while precipitating As, Sb, and Bi from the organic phase. Separation of the sulfide precipitates is made by continuous washing with H_2SO_4 followed by filtration. The sulphuric acid is recycled and the organic phase (stripped of As, Sb, and Bi) is ready for the stripping of iron.

In order to remove any iron remaining in the organic phase, a second strip is conducted using water-soluble complexing agents. These may include oxalic acid, organophosphorus acids or HCl.

The difficulty in stripping XI-104 has made this reagent undesirable in the present application. The possibility of the having to strip the organic at elevated temperature under an overpressure of hydrogen sulphide is not an attractive alternative. It is the authors' understanding that Henkel is seeking to modify the strength of the extractant to increase strippability. The mechanism of modification is not known.

Thio Carbamic Acids

It is reported that diethyldithiocarbamate will extract arsenic(III) from acid solutions (Halina and Henryk, 1971, Puttemans and Massart, 1982 and Byr'ko et al., 1983). Unfortunately the thio carbamic acid also will strongly extract copper. This probably makes this group of reagents unsatisfactory for the purification of copper electrolytes.

Thio Phosphoric Acids

Sergeeva et al. (1973) have reported the extraction of arsenic(III) from acid solutions using di-1-ethylhexyldithiophosphoric acid. As in the case of the thio carbamic acids, it is likely that copper would also be strongly extracted by this reagent. Schimmel et al. (1985) have described the extraction of arsenic from phosphoric acid solutions.

2.2.1.3 Basic Extractants

No basic extractants have been reported to extract arsenic in acid sulphate solutions.

2.2.1.4 Chelating Extractants

Demopoulos and Gefvert (1984) have reported that a mixture of Kelex 100 and D2EHPA extracted only 3% of the arsenic from a copper electrolyte bleed solution. No other chelating extractants have been reported to extract arsenic in acid sulphate solutions.

2.2.2 Antimony Extraction

2.2.2.1 Solvating Extractants

The phosphorus oxygen based solvating extractants are generally weak antimony extractants from acid sulphate solutions. For example, TBP extracts less than 20% of the contained antimony in the MHO process for arsenic removal.

Marinkina et al. (1982) have shown that antimony can be selectively removed from a sulphuric acid solution using octylmercaptan. Selectivity for antimony over copper is claimed.

Guerriero and Vittadini (1989) have reported that polyhydroxyalcohols selectively extract antimony out of acidic aqueous solutions. Particularly useful alcohols reported for antimony extraction include octane-1,2-diol, decane-1,2-diol, dodecane-1,2-diol, tetradecane-1,2-diol and hexadecane-1,2-diol. The extraction of antimony was reported to be very sensitive to acid concentration. The higher the acid content, the more favourable the extraction of antimony.

Shoji et al. (1974) have reported that antimony and arsenic are extracted with dithizone under acid conditions.

Moriya et al. (1988) have reported antimony extraction from chloride electrolytes using mixed monoalkyl, dialkyl and trialkyl phosphate esters.

2.2.2.2 Acid Extractants

Yukhin et al. (1979) showed that antimony (III) could be recovered from mineral acid solutions using di-2-ethylhexyldithiophosphoric acid. Unfortunately, copper is also very strongly extracted by this reagent.

2.2.2.3 Basic Extractants

No basic extractants were reported to extract antimony from an acidic environment.

2.2.2.4 Chelating Extractants

Demopoulos and Gefvert (1984) reported that a mixture of Kelex 100 and D2EHPA extracted 70% of the antimony from a copper electrolyte bleed solution. No other chelating extractants have been reported to extract antimony in acid sulphate solutions.

Rao and Ramesh (1987) observed that a mixture of LIX 26 and MIBK extracts antimony from a slightly acidic solution. Unfortunately, LIX 26 is also a strong extractant for copper. Ramesh and Rao (1988) also examined LIX 622 and MIBK and found that antimony was not extracted.

2.2.3 Bismuth Extraction

2.2.3.1 Solvating Extractants

The phosphorus oxygen based solvating extractants are generally weak bismuth extractants from acid sulphate solutions.

Nikitin et al. (1976) indicated that petroleum sulphoxides extract bismuth from nitric acid solutions. The sulphoxides are unfortunately also very strong extractants for copper from the same solutions.

2.2.3.2 Acid Extractants

Min and Hwang (1978) reported that carboxylic acid extractants could favourably extract bismuth at pH values above 1.0. Carboxylic acids do not appear to be strong enough to extract bismuth out of a concentrated acid solution. De and Ray (1972) also reported quantitative extraction of bismuth by the carboxylic acid SRS-100 at pH 7-9.

Buscarons and Canela (1974) reported that bismuth was quantitatively extracted with hexahydrocupferron (N-nitroso-N-cyclohexylhydroxylamine) at pH values in the range 0-11. Copper was more weakly extracted.

Yukhin et al. (1975, 1979 and 1984) have reported the extraction of bismuth and antimony with napthenic, thionapthenic, aliphatic monocarboxylic, alkylphosphoric, dialkylthiophosphoric and dialkyldithiophosphoric acids and alkylmercaptans.

2.2.3.3 Basic Extractants

No basic extractants were reported to extract bismuth from an acidic environment.

2.2.3.4 Chelating Extractants

Demopoulos and Gefvert (1984) observed that a mixture of Kelex 100 and D2EHPA extracted only 10% of the bismuth from a copper electrolyte bleed solution. No other chelating extractants have been reported to extract bismuth in acid sulphate solutions.

2.3 ION EXCHANGE

2.3.1 Introduction

Ion exchange is an analogous technique to solvent extraction. The organic solution used in solvent extraction is replaced by a bead of resin with functional groups attached to the resin matrix. These functional groups are able to exchange ions with an aqueous solution. Like solvent extraction, the applications of ion exchange have been increasingly numerous.

2.3.2 Chemistry of Ion Exchange

The chemistry of ion exchange is best described by treating separately the chemistries of the resin substrate and the active groups.

2.3.2.1 The Resin Matrix

In ion exchange, the resin substrate is usually an organic polymer which is generated in bead form (0.5-2 mm dia). One common type of resin is polystyrene-divinylbenzene. Polystyrene forms linear polymers which are then crosslinked to provide structural strength as shown in Figure 2.9. Gel type resins (microporous) result when only styrene and divinylbenzene are used in the synthesis. When an inert material such as toluene is added during polymerization and evaporated after bead formation, then a macroporous bead results. Macroporosity typically enhances the kinetics.

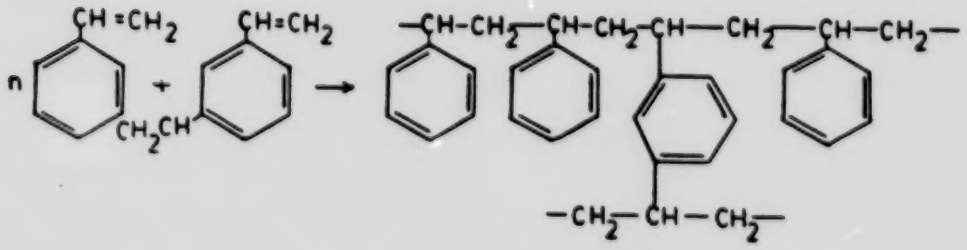


Figure 2.9. Polymer formation of styrene - divinylbenzene resin matrix.

The important physical properties which impact the use of ion exchange resins are swelling, mechanical strength, abrasion resistance, rate of exchange, exchange selectivity and exchange capacity. Each of these depend to some extent on the degree of crosslinking. A low degree of

crosslinking permits the resin to swell considerably, sometimes to ≈ 4 times its dry volume. Swelling is caused by the absorption of water into the resin structure. Water molecules will tend to hydrate the functional groups. This has the added disadvantage of lowering the exchange capacity. A resin with a low degree of crosslinking will also break or abrade more easily under mechanical or osmotic shock induced stresses. In contrast, higher rates of exchange are achieved with a low degree of crosslinking. As a tradeoff among these factors, the amount of crosslinking for polystyrene-divinylbenzene (DVB) resins is usually in the range of 4-8% DVB.

Other organic polymers are also employed as resin matrices. These include phenol formaldehyde, polyacrylic and poly(vinylimidazole) resins. The current interest in chelating ion exchangers has provided renewed interest in developing new matrix materials that may also participate in the chelation reaction.

2.3.2.2 Functional Groups

The active groups fall into basically the same categories as the extractants of solvent extraction.

Strong and Weak Acid Ion Exchangers

Cation exchange is carried out by the use of strong or weak acid ion exchangers. Sulphonic acid type exchangers with the functional group $-SO_3H$ extract cations at low pH but are relatively unselective. The weak acid resin of the type $-CO_2H$ is analogous to the carboxylic acid extractant. This resin type loads at moderate pH (>4) and is somewhat more selective. The weak acid resin of the type $=PO_2H$ is analogous to the phosphoric acid extractant. Again, the resin is limited to pH values of >4 and has some degree of selectivity. Note that the pH limitation of weak acid ion exchangers is due to the stability of the protonated weak acid group at high acidities.

Strong and Weak Base Anion Exchangers

The weak and strong base anion exchangers are based on amine derivatives. Weak base resins with the functional groups $-NR_2$, $-NHR$ and $-NH_2$ must be protonated to exchange ions. The useful pH range is therefore approximately 0-10. Strong base resins are analogous to quaternary ammonium extractants with the group $-NR_3X$ and extract anions efficiently over the entire pH range of 0-14. The weak acid exchangers are generally more selective than the strong acid exchangers. Table 2.5 lists some of the important properties of the strong and weak acid and base exchangers.

Chelating Ion Exchangers

One of the interesting recent developments in hydrometallurgical applications of ion exchange has been the commercial introduction of a new series of chelating resins. These resins have demonstrated a high degree of selectivity for some metal ions that was unavailable with the conventional exchangers. Table 2.6 lists some of the chelating resins with their properties (Melling and West, 1984). The imidodiacetic acid and aminophosphonic acid resins exchange cations.

Ion Exchange Analogues

There are three other ion exchange materials that warrant brief mention. The first is the development of solvent impregnated resin beads. In this technique, solvent extraction reagent mixtures are absorbed into macroporous resin beads. This technique has the advantage of reduced solvent losses relative to conventional solvent extraction processes and increased selectivity over conventional resins. The second material that should be mentioned is activated carbon. This material has found wide application in gold recovery circuits, selectively adsorbing the aurocyanide species. The mechanism of extraction is not well characterized (i.e., not strictly an anion exchanger) but the technology for adsorption and elution have been well developed. Inorganic ion exchanger materials form the third grouping. It has been found that aluminosilicates (clays and zeolites), heteropoly acid salts and hydrous oxides of polyvalent metals, have some interesting ion exchange properties. For example, zirconium phosphate has a high selectivity for rubidium and cesium over the other alkali and alkaline earth metals.

Table 2.5. Some Generalized Properties of Strong and Weak Acid and Base Resins (Grimshaw and Harland, 1975).

Resin type	Matrix and functional group	Approx. capacity (keq/m^3)	Max. temp. (°C)	pH range	Commercial resins
Strong Acid (Gel)	Crosslinked polystyrene $-SO_3H$	1.9	120	0-14	Zerolit 225 Amberlite IR-120 Lewatit S-100
Weak Acid (Gel)	Crosslinked polyacrylic $-CO_2H$	4.1	100	4-14	Zerolit 236 Amberlite IRC-84 Duolite CC3
Strong acid (Macroporous)	Crosslinked polystyrene $-SO_3H$	1.75	120	0-14	Zerolit 625 Amberlite 200 Lewatit SP-120
Strong base (Gel)	Crosslinked polystyrene $-NR_3X$	1.2	60	0-14	Zerolit FF(ip) Amberlite IRA-400 Duolite A101D
Weak base (Gel)	Crosslinked polystyrene $-NR_2$	1.2	70	0-9	Zerolit H (ip) Amberlite IRA-45 Wofatit AD-41
Strong base (Macroporous)	Crosslinked polystyrene $-NR_3X$	1.0	60	0-14	Zerolit MPF Amberlite IRA-900 Lewatit MP-500
Weak base (Macroporous)	Crosslinked polystyrene $-NR_2$	1.6	80	0-9	Zerolit MPH Amberlite IRA-93 Lewatit MP-62

Table 2.6. Chelating Ion Exchangers (Melling and West, 1984).

Functional Groups	Commercial Designation	Manufacturer
Imidodiacetic acid $-CH_2NCH_2(CO_2H)_2$	TP-207 XE-718 ES-466	Bayer Rohm and Haas Duolite
Picolylamine $-N(CH_2C_5NH_4)_2$ $-N(CH_2C_5NH_4)C_2H_4OH$	XFS-4195 XFS-4196	Dow Dow
Aminophosphonic acid $-CH_2-NH-CH_2-PO(OH)_2$	C-467	Duolite

2.3.3 Arsenic Extraction

There are no known commercial applications of arsenic ion exchange from copper electrolytes. The following is a description of research that has gone on in arsenic ion exchange.

2.3.3.1 Strong and Weak Acid Ion Exchangers

Dadabaev et al. (1970) reported that a strong acid resin (sulphonic acid type) extracted only small amounts of arsenic(V) from an acid solution. Kabanova et al. (1987) described a process whereby an arsenic containing copper-nickel sulphate, sulphuric acid solution was passed through a strong acid resin bed. Arsenic was not extracted.

Ueno (1977) described a patent in which arsenic oxy acid ions in water are selectively adsorbed on a cation exchange or cationic chelating resin containing transition metal ions or absorbed on porous inert particles (containing a transition metal hydroxide). The author stated that the process could be effective in eliminating small amounts of arsenic in wastewater. The experiment(s) to simulate arsenic removal consisted basically of two steps: 1) 300 mL of a solution of 0.05 M $Fe(NO_3)_3$ at pH = 3 is passed through a resin column containing such a cation exchanger (unidentified by the author) and 2) 3 liters H_2O (pH = 9.9) containing 10 ppm As(III) is filtered through the ion exchange column at 20 mL/h to remove arsenic. After washing the resin column with water and 100 mL of 2N HCl, the resulting eluate analyzed 29 mg As and 223 mg Fe.

It appears as though the technique is suitable for removal of trace amounts of arsenic, but unfortunately further evaluation of this particular ion exchange method under more severe conditions (e.g. acidity, etc.) and a higher load of contaminating species was not done.

2.3.3.2 Strong and Weak Base Ion Exchangers

Sengupta et al. (1988) have shown that arsenic (V) can be removed from neutral waste waters using strong base anion exchangers (tri-propyl quaternary amine functionality on a polystyrene resin). Other authors have investigated similar systems (Lee and Rosehart, 1972, Sandhu and Nelson, 1979, Stergarsek et al., 1989, Fox, 1989 and Fox and Sorg, 1987). Although effective at neutral to alkaline pH, these resins are unlikely to be effective under highly acidic conditions prevailing in copper electrorefining.

2.3.3.3 Chelating Ion Exchangers

No chelating exchangers have been reported to extract arsenic in acid sulphate solutions.

2.3.3.4 Other Ion Exchangers

Unitika Ltd. (Iwaya, 1983) patented an ion exchange resin capable of removing arsenic(III) from wastewater.

The resin consists of a phenol polymer matrix with amino-polyalcohol functional groups.

$$CH_2N(R)CH_2[CH(OH)]_nCH_2OH \text{ moiety}$$

where R = H or C_{1-5} alkyl and n = 1-6.

Iwaya (1987) also discusses the adsorption characteristics of Amberlite IRA-743 for the removal of As^{3+} from solution. The adsorption capacity was determined to be 30 mg As^{3+} per mL of resin.

The removal of arsenic from sulphuric and/or hydrofluoric acid containing solutions typically from gas scrubbers in foundry operations was patented by Gerish et al. (1985). The German patent described the use of ion exchangers based on styrene-divinylbenzene copolymers with sulfhydryl groups for elimination of the arsenic from acid concentrations of 1-100 g/L. Resin regeneration is made possible with an alkaline solution (0.1-0.3 N NaOH, NH_3). In the experiments conducted by Gerish and his coworkers, a 0.001-1.0 N H_2SO_4 solution with an arsenic content of 4.1 g/L was passed upwards through an ion exchange column. Maxiumum capacity of the ion exchanger was

measured at 18 g As/l, although this value is independent of H_2SO_4 concentrations between 0.1 to 1.0 N. However, lowering the acidity caused a decrease in the resin's adsorption capacity. As was proposed by the authors, 1 N NaOH effectively regenerated the resin.

Lyubman et al. (1976, 1980, 1981) discuss the use of a macroporous pyrocatechol-formaldehyde polymer for arsenic (III) extraction. The authors claim that a copper refining electrolyte may be pre-treated with sulphur dioxide to reduce all arsenic to the trivalent oxidation state. The solution is then passed through the resin bed to load arsenic. Elution is accomplished with water.

Zharmenov et al. (1984) have reported that an electrodialysis cell can be used to separate copper and nickel sulphate from arsenic in solution. The cell uses alternate anionic and cationic ion exchange membranes.

Rozmanov et al. (1970) reported a survey of 26 resins for arsenic removal from ~ 1 M H_2SO_4 solutions. The conclusion of the paper was that none of the resins could be recommended for practical use.

2.3.4 Antimony Extraction

Antimony is commercially ion exchanged from copper electrolytes. The following is a description of research and practice for antimony removal from copper electrolytes.

2.3.4.1 Strong and Weak Acid Ion Exchangers

Kholmanskikh et al. (1971, 1973) have described antimony extraction with a phosphate based cation exchanger. Antimony was quantitatively removed from a copper electrolyte at temperatures of 50-70 °C from a solution containing 100-200 g/L sulphuric acid. The resin was referred to as KFP-8 or KFP-12 without any detail on the exact functionality or resin matrix. The resin also adsorbed small amounts of ferric ion and bismuth from the copper electrolyte. Antimony elution was accomplished with 3-6 normal hydrochloric acid.

Cunningham et al. (1977) have reported that strong base cation exchangers (sulphonic acid type) can extract antimony from weakly acidic solutions.

2.3.4.2 Strong and Weak Base Ion Exchangers

Strong and weak base ion exchangers have not been studied or applied for antimony removal from strong acid solutions.

2.3.4.3 Chelating Ion Exchangers

Lyubman et al. (1976) observed that antimony can be removed from copper electrolytes using a pyrocatechol macroporous resin designated PK-S. The pilot scale flowsheet is shown in Figure 2.10. The flowsheet is complicated. Some coextraction of copper, nickel and arsenic must be dealt with in the process. The final product is antimony metal.

Shibata and coworkers (1987) described the Tamano Chelating Resin (TCR) Adsorption Process that incorporates a chelating resin for the selective removal of antimony and bismuth from copper electrolytes. This is applied jointly with a surface electrolyte bleed technique for the electrorefining cells in order to give improved purification. The impurities are eluted using HCl, resulting in a concentrated antimony chloride product. The chelating resin, Unicellex UR-3300, is produced by Unitika Ltd. of Japan and has an amino phosphonic acid functionality on a phenolic resin matrix. The resin's selectivity for metal ions is reported to be :

$Sb^{3+} > Bi^{3+} > Sb^{5+} > Fe^{3+} > Mo^{6+} > Cu^{2+} > Fe^{2+} > Mn^{2+} > Ni^{2+}$.

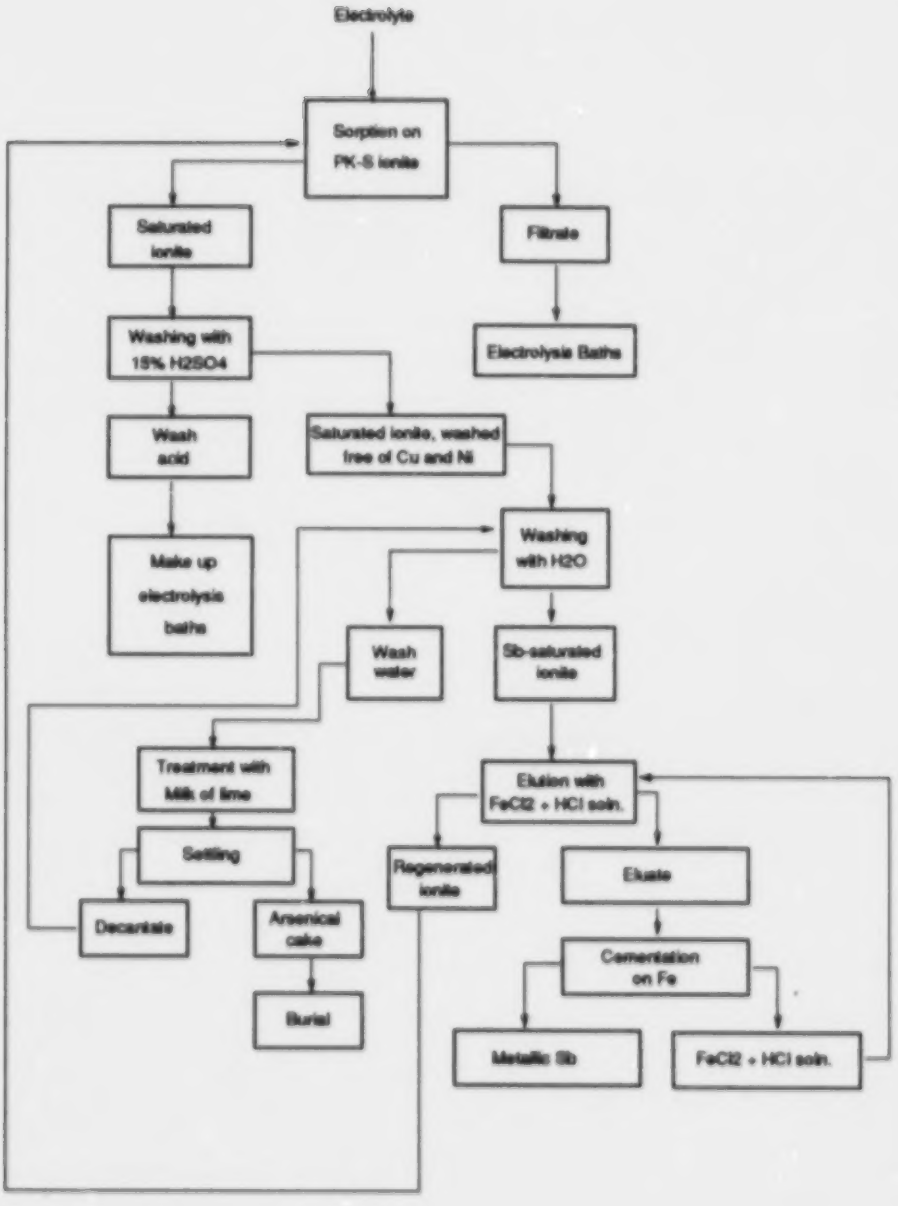


Figure 2.10. Diagram of Antimony Extraction from Copper Electrolyte (Lyubman et al. (1976)).

Figure 2.11 illustrates the TCR Process as two main sections: 1) the chelating section and 2) the evaporation section. In the chelating section the primary steps are adsorption and desorption for which the cycling time is solely dependent on the amount of impurities present. During

Table 2.7. Segregation of Copper and Sulphuric Acid in Cell Electrolyte

	Component (g/L)					
Depth Below Surface (mm)	Cu	H_2SO_4	As	Sb	Bi	Ni
10	35.2	192.5	3.24	0.40	0.088	14.2
30	37.4	191.5	3.24	0.40	0.089	14.2
50	42.2	189.2	3.24	0.40	0.089	14.2
500	43.2	186.4	3.25	0.41	0.091	14.3
1000	45.0	183.5	3.26	0.39	0.090	14.1
Outlet Electrolyte	45.2	183.3	3.26	0.40	0.092	14.1

adsorption, the electrolyte from the circulation tank is passed through the chelating resin column or tower. In desorption, antimony and bismuth are eluted by HCl in a series of four steps. The system is initially purged of electrolyte by replacement with water and then it receives recycled HCl for preliminary desorption of the contaminants. Fresh HCl is then added for complete elution of antimony and bismuth and also, for resin regeneration. The final step consists of a secondary water purge to rid the section of hydrochloric acid and to prepare for the treatment of the next batch of electrolyte. The impurities are converted to their chloride form and sent to the HCl evaporation section.

In the evaporation section the HCl is evaporated, reconcentrated to a 6 N level and recycled to the chelating section. Antimony, bismuth and other heavy metals are further recovered in the form of a concentrated solution. At this point in the process, the antimony concentration in solution exceeds 100 g/L.

The chelating resin is fairly durable and there is no evidence of its deterioration since its initial use in January, 1984. Overall adsorption capacity of the Unicellex UR-3300 resin remains high. The percentage of impurity removal is largely dependent on the concentration of impurities present in the electrolyte and is independent of the apparent copper concentration in solution. An average of 50 kg of antimony and 7 kg of bismuth are extracted daily by the TCR Process.

Patents assigned to Unitika (Nagai and Echigo, 1985, 1986) have reported further data on antimony and bismuth removal from copper electrolytes UR-3300. Tanaka et al. (1985) have reported on the use of UR-3300 to remove antimony and bismuth from lead electrolytes (lead fluosilicate, fluosilicic acid).

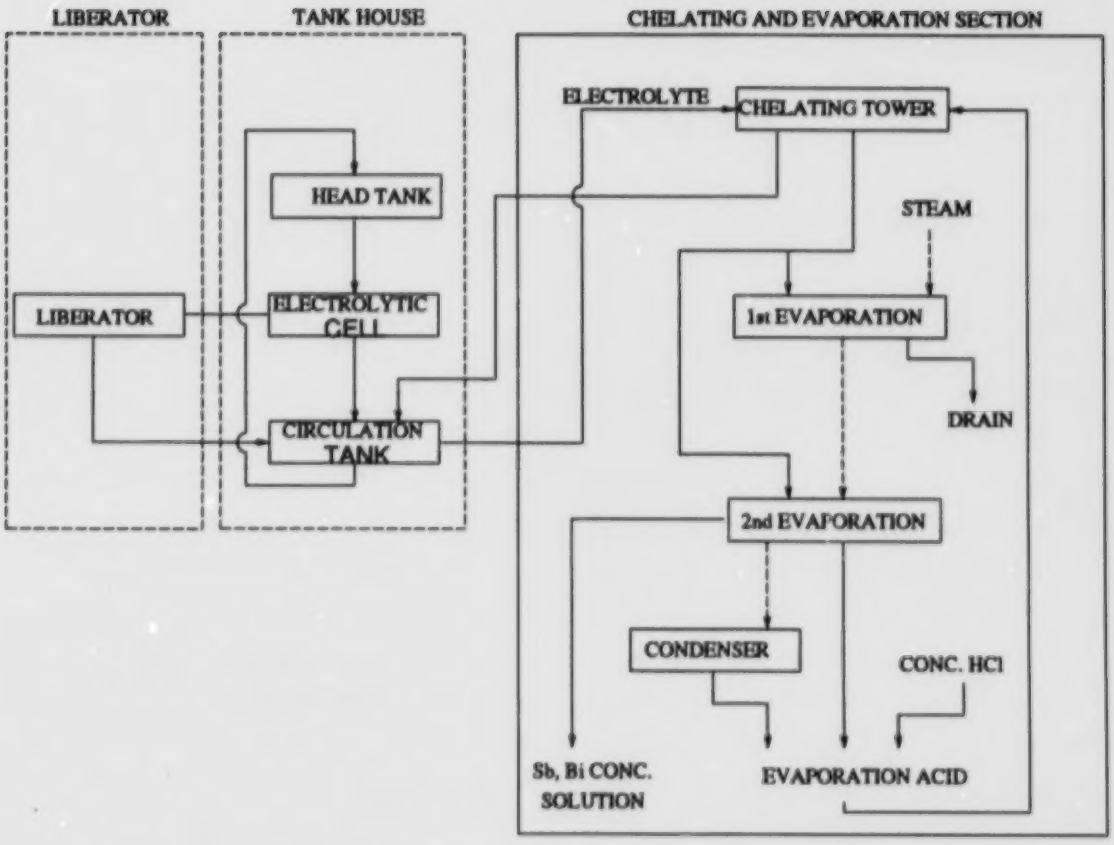


Figure 2.11. Flow Connecting TCR Process to Tank House and Liberator Section.

Sasaki et al. (1991) described a new antimony removal process for copper electrolyte at the Hitachi Refinery (Nippon Mining Co. Ltd.), which has operated successfully since August, 1989. Up to 1.5 tpm of antimony is removed from two ion exchange columns. It is understood that this process has also been installed in the Saganoseki refinery operated by Nippon Mining Company. Antimony is adsorbed using a chelating ion exchange resin that is highly selective for Sb over Cu. The resin is made by the Miyoshi Oil and Fat Company under the tradename Eporous MX-2. The resin contains a phosphonic acid functional group on a polystyrene, divinyl benzene resin matrix. This resin functionality is the same as that of UR-3300. The only difference between the resins is the resin matrix. The antimony removal process operates independently from other purification methods. Elution is possible with HCl and the first eluate is separated into two parts. The portion having a higher concentration of antimony is removed from the system, whereas the second portion containing a sufficient amount of HCl is re-used in the next stage of elution. Regeneration of the

resin requires only two steps: 1) elution with HCl and 2) rinsing with water. The hydrochloric acid solution containing antimony is neutralized with lime. The neutralization residue (predominantly antimony oxide) is sent to a lead smelter for metal recovery. Sasaki (1991) reports that some bismuth reports to the antimony residue (54.4% Sb and 2.39% Bi). The original solution contains about 0.4 g/L Sb and 0.35 g/L Bi. Although Sb/Bi selectivity results have not been reported by Nippon, it is obvious from the large Sb/Bi ratio in the residue that the resin is more selective for antimony than bismuth by a factor of about 20-25.

2.3.4.4 Other Ion Exchangers

Petkova et al. (1981) have examined antimony extraction from copper electrolyte using metastannic acid - polyacrylnitrile granulated pellets. The resin was selective for antimony over other metals. Loadings of 80-100 mg of antimony per gram of metastannic acid were achieved. The metastannic acid was regenerated with HCl.

At the Sumitomo Niihama Copper Refinery (SNCR) high levels of antimony can be efficiently eliminated from the copper electrolyte through contact with activated carbon (Toyabe et al., 1987). This technique is part of a three-stage process designed to control impurity levels during electrolysis. The activated carbon allows selective adsorption of the antimony over arsenic and bismuth. Figure 2.12 is a flow sheet illustrating the overall purification process. Table 2.8 summarizes the metal removal results of the commercial operation. Impurity removal is favoured at lower temperature.

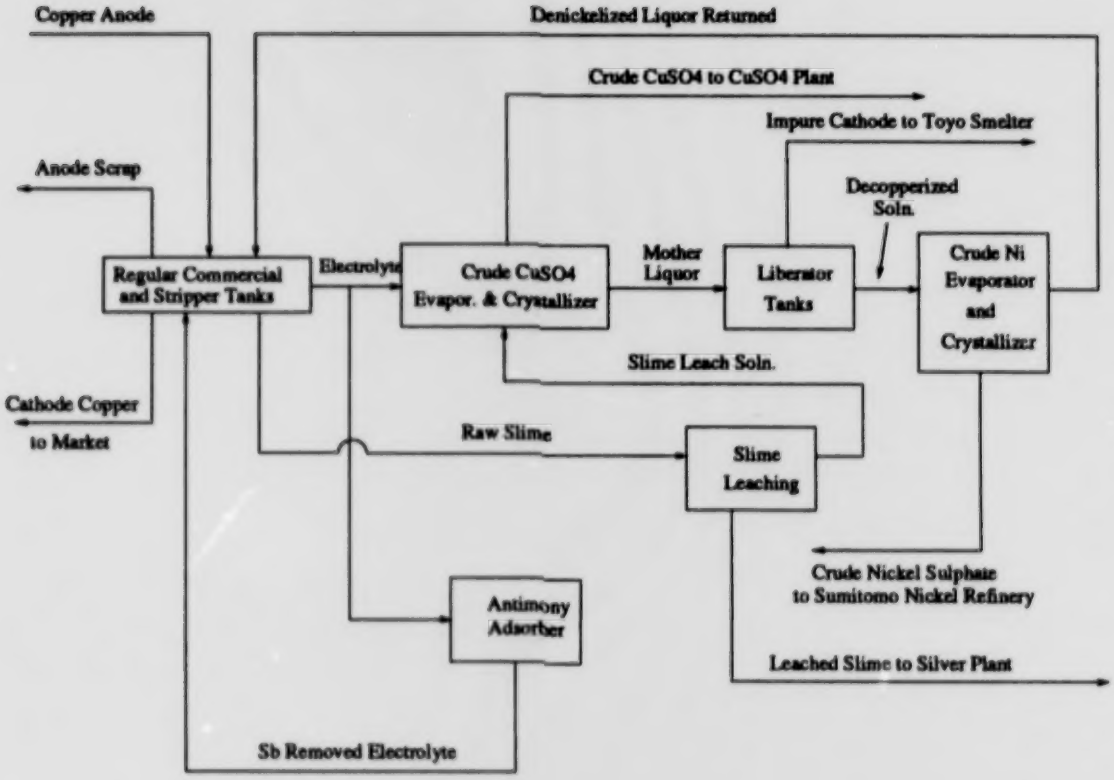


Figure 2.12. Flowsheet of the Purifying Process for Copper Electrolyte in SNCR.

Table 2.8. The Relationship between the Extent of Separation of Impurities and the Temperature of the Solution.

Conditions		Analyses (g/L)			Degree of Removal (%)		
Electrolyte	Temp. of Electrolyte	Sb	As	Bi	Sb	As	Bi
Inlet Soln.	50°C	0.58	6.4	0.60	--	--	--
	Room Temp. (20-25°C)	0.58	6.4	0.60	--	--	--
Outlet Soln.	50°C	0.09	5.9	0.55	84.5	7.8	8.3
	Room Temp. (20-25°C)	0.05	5.7	0.52	91.4	10.9	13.3

2.3.5 Bismuth Extraction

Bismuth ion exchange has been reported by a number of workers. The following subsections summarize the results.

2.3.5.1 Strong and Weak Acid Ion Exchangers

Adsul, et al. (1987) discussed the extraction of bismuth from sulphide ores, concentrates and high purity Cu, Ag, and Ag-Cd alloy. Extraction studies were made under high acidity levels using Chelex 100 in the H^+ form. Chelex 100 is a monofunctional, chelating ion exchanger consisting of styrene divinylbenzene copolymers with paired iminodiacetate ions. The iminodiacetate ions act as chelating groups to successfully bind polyvalent metal ions. A comparison of distribution ratios for bismuth and other metal cations in 0.25 M HNO_3 by the batch method revealed good separability of Bi(III) over Fe(III) and Cu(II) (see Table 2.9). Elution is possible with 2 M nitric acid.

Table 2.9 Batch Method Kd Values for Chelex 100 (Adsul et al., 1987)

CATION	$[HNO_3]$, M	K_d
Bi(III)	0.10	$> 10_4$
	0.20	6000
	0,25	2700
	0.30	1400
	0.40	550
	0.50	250
	1.0	15
	2.0	nil
Au(III)	0.25	$> 10_4$
Mo(VI)	0.25	$> 10_4$
Hg(II)	0.25	1950
In(III)	0.25	56
Fe(III)	0.25	30
Cu(II)	0.25	10
Ga(III)	0.25	10
Ag^+, Zn^{2+}, Cd^{2+}, Pb^{2+}	0.25	< 10

2.3.5.2 Strong and Weak Base Ion Exchangers

No references to the application of these exchanger types were located.

2.3.5.3 Chelating Ion Exchangers

Masuda et al. (1985) of Dowa Mining Company successfully used a chelating ion exchange resin to remove impurities such as Pd, Bi, Pb and Cu from silver electrorefining solutions. A second ion exchange resin was then employed to contact the treated solution for the purpose of lead removal. Elution and regeneration of the resin are carried out effectively with an inorganic acid. Table 2.10 gives an analysis of the initial composition of the silver electrolyte. In a first step, 600 mL of the electrolytic solution is treated with Unicellex UR-50 (a chelating ion exchange resin with amino carboxyl groups) to give a treated solution (650 mL). This solution is then adsorbed using Unicellex UR-3300T (a chelating ion exchange resin having aminoalkylphosphonic acid groups) to give a final purified solution .

Table 2.10. Electrolyte Composition During Stages of Treatment with UR-50 and UR-3300T Resins.

	Composition (g/L)				
	Ag	Pb	Pd (mg/l)	Cu	Bi (mg/l)
Feed Electrolyte	36.2	1.93	8	1.87	3
Treated Sol'n. (UR-50)	34	1.65	< 0.1	< 0.01	< 0.1
Final Sol'n. (UR-3300)	33.8	0.01	< 0.1	< 0.01	< 0.1

2.3.5.4 Other Ion Exchangers

IBC Advanced Technologies has reported the development of a reagent designated Superlig that is selective for bismuth removal from copper electrolytes. The reagent formulation has not been made public. However, it is generally understood to be a crown ether compound on a silica support. Superlig is designed to be loaded into fixed bed columns similar to ion exchange columns. IBC claims to be able to reduce bismuth in electrolyte to less than 5 ppm. Bismuth stripping is accomplished with sulphuric or hydrochloric acid.

3 SOLVENT EXTRACTION SCREENING EXPERIMENTS

3.1 INTRODUCTION

Based on the literature review and discussions with reagent suppliers, a number of solvents was selected for laboratory study. The laboratory study was conducted in three stages. The first stage consisted of a series of shakeout tests using the full range of solvents to identify the most promising reagents. McCabe-Thiele Distribution Isotherms were then constructed for the most promising reagent - metal combinations. Finally, the solvents were stripped.

3.2 EXPERIMENTAL METHODS

Synthetic electrolytes were prepared from reagent grade chemicals. $CuSO_4.5H_2O$ and concentrated H_2SO_4 were used to prepare the electrolyte matrix. As_2O_3 (arsenic (III)) or Na_2HAsO_4 (arsenic (V)) were dissolved in hot concentrated H_2SO_4 and added to the copper sulphate solution. Antimony was added as $Sb_2(SO_4)_3$. Bismuth was added as Bi_2O_3.

Solvent extractants were either used as full strength reagents or diluted with a diluent. The diluent employed was Exxol D-80, an aliphatic solvent that has been widely used in the copper industry.

Shakeout tests were used for both the screening and the McCabe-Thiele studies. Shakeout tests were performed using 250 mL separatory funnels. Organic and aqueous solutions were placed into the separatory funnels. The funnels were then placed in a thermostatted shaking device. After reaching temperature, the phases were mixed for a prescribed length of time. For all experiments, mixing continued until equilibrium was established. The phases were then allowed to separate at temperature. The phases were then decanted and filtered. The phase volumes were measured as accurately as possible.

3.3 ANALYTICAL TECHNIQUES

Aqueous Solution Analysis

It was initially hoped that arsenic, antimony and bismuth concentrations could be measured using multi-element ICP. Much effort was devoted toward development of such a technique. Unfortunately, this effort was not successful due to equipment limitations. Consequently, all arsenic, antimony and bismuth analyses were completed using Flame Atomic Absorption Spectrophotometry (AAS). The difficulty of performing these assays in-house necessitated the contracting out of these analyses to Chemex Labs (North Vancouver, B.C.).

Copper concentrations in solution were measured in-house using Flame AAS. Acid concentrations were measured by titration with NaOH solutions in the presence of a metal ion complexing agent (oxalic acid).

It was initially hoped that As(III)/As(V) speciation could be detected using ion chromatographic techniques. For the purposes of a screening study, it was concluded that such speciation was unnecessary. Finally, it was assumed that the arsenic oxidation state did not change significantly after stock solution preparation (i.e., As(III) was stable in a sealed container).

Organic Solution Analysis

Organic solutions were not analyzed for metal concentrations. For solvating extractants, acid levels were determined by titration with NaOH in 80% propanol solutions.

3.4 SHAKEOUT EXPERIMENTS

Two series of screening tests were performed. The first series was designed to measure the degree of impurity pickup from solutions of variable acidity at variable temperature. Stock solutions containing approximately 10 g/L Cu, 5 g/L As (III or V), 0.1 g/L Sb(III), 0.01 g/L Bi (III) and 100, 200, 300 or 400 g/L H_2SO_4 were prepared. These stock solutions were contacted at an aqueous to organic ratio of 1 at either 25 or 50 °C with the solvents of interest. Table 3.1 summarizes the solvents that were examined.

Table 3.1. Solvent Extractants Examined in the Shakeout Tests.

Extractant	Manufacturer	Solvent Class
Tri-butyl-phosphate (TBP)	Bayer	Solvating Extractant
Di-butyl-butyl-phosphonate (DBBP)	Albright and Wilson	Solvating Extractant
Di-pentyl-pentyl-phosphonate (DPPP)	Albright and Wilson	Solvating Extractant
Cyanex 923 (Mixture of trialkyl phosphine oxides)	American Cyanamid	Solvating Extractant
Cyanex 925 (Sterically hindered phosphine oxide)	American Cyanamid	Solvating Extractant
Cyanex 302 (monothiophosphinic acid)	American Cyanamid	Acid Extractant
Mono 2 ethyl hexyl phosphoric acid (M2EHPA)	Albright and Wilson	Acid Extractant
LIX 1104 (Hydroxamic Acid)	Henkel	Acid Extractant
LIX 1104 Modified (Hydroxamic Acid)	Henkel	Acid Extractant
Versatic Acid (Versatic 10)	Shell	Acid Extractant
Kelex 100	Sherex	Acid Chelating Extractant

3.4.1 Results

The results of the arsenic, antimony and bismuth extractions in the screening study are summarized in Tables 3.2-3.4. The only solvent that extracted significant copper under the conditions studied was Cyanex 302. This solvent extracted 91% of the copper at 100 g/L H_2SO_4 and 83% of the copper at 400 g/L H_2SO_4. The solvating extractants all extracted acid to some extent. A complete analysis of acid extraction is included in the section reporting McCabe Thiele data.

Table 3.2. Arsenic Extraction by Various Extractants at Variable Acidity and Temperature.

Extractant	Vol. %	Temp. (C)	time (min.)	sample [H2SO4] g/L	feed [As] g/L	sample [As] g/L	% As Extracted	Oxid. state
TBP	100	50	20	102.31	5.84	5.68	12.47	3+
				198.26	5.84	5.72	13.81	
				275.61	5.92	5.76	16.32	
				377.44	5.84	5.76	17.15	
TBP	100	25	20	99.87	4.04	3.52	19.84	3+
				194.84	3.92	3.60	17.35	
				273.65	3.96	3.52	20.89	
				359.32	3.92	3.60	21.94	
TBP	100	50	20	423.94	3.76	3.84	13.19	3+
TBP	100	50	20	202.88	2.40	1.92	28.00	5+
				293.94	2.28	1.36	47.51	
				376.94	2.40	1.04	62.73	
TBP	100	25	20	195.96	2.40	1.40	47.50	5+
				281.97	2.28	0.96	63.79	
				358.48	2.40	0.80	72.00	
DPPP	100	50	20	99.83	4.04	3.56	18.93	3+
				192.71	3.92	3.40	21.07	
				274.91	3.96	3.44	21.82	
				353.14	3.92	3.44	22.78	
DPPP	100	25	20	97.59	4.04	3.92	11.70	3+
				187.11	3.92	3.80	13.72	
				269.86	3.96	4.16	8.61	
				348.34	3.92	4.00	13.27	
DPPP	100	25	20	184.86	2.16	0.84	65.39	5+
				266.56	2.08	0.64	73.54	
				346.26	2.24	0.48	82.00	
CYANEX 925	100	25	20	151.05	2.16	0.48	80.22	5+
				229.16	2.08	0.56	76.31	
				313.33	2.24	0.72	71.71	
CYANEX 923	100	50	20	69.03	5.84	4.72	28.88	+3
				138.05	5.84	5.00	26.37	
				213.44	5.92	5.04	27.29	
				288.83	5.84	5.24	21.04	
CYANEX 923	75	50	20	79.80	5.84	5.04	21.47	3+
				152.74	5.84	5.12	21.10	
				231.06	5.92	5.08	22.77	
				315.75	5.84	5.20	19.86	
CYANEX 923	100	25	20	67.05	4.04	3.76	17.17	3+
				132.36	3.92	3.28	25.53	
				211.09	3.96	3.76	16.44	
				292.54	3.92	3.81	14.78	

CYANEX 923	100	25	20	132.48	2.16	0.36	86.00	5+
				210.51	2.08	0.44	81.81	
				291.74	2.24	0.48	81.57	
DBBP	100	50	20	99.87	5.84	5.20	24.32	3+
				185.54	5.84	5.24	25.53	
				264.84	5.92	5.16	32.01	
				341.70	5.84	5.36	28.59	
DBBP	100	25	20	99.83	4.04	3.80	21.93	3+
				181.78	3.92	4.20	13.21	
				262.74	3.96	4.24	15.41	
				340.72	3.92	4.24	16.71	
DBBP	100	25	20	180.22	2.40	0.88	70.30	5+
				265.76	2.28	0.72	75.05	
				334.40	2.40	0.68	78.18	
CYANEX 302	25	50	20	120.69	5.84	5.20	15.41	3+
				211.34	5.84	5.20	13.63	
				308.68	5.92	5.20	15.68	
				402.31	5.84	5.16	13.41	
M2EHPA	50	50	20	116.97	5.84	5.52	12.10	3+
				201.65	5.84	5.60	10.82	
				299.25	5.92	5.52	13.28	
				392.62	5.84	5.52	11.15	
LIX 1104	20	50	20	107.03	5.84	3.84	36.88	3+
(UNMODIFIED)				198.92	5.84	3.68	39.51	
				297.51	5.92	3.36	45.51	
				390.64	5.84	3.24	46.74	
LIX 1104	20	25	20	193.84	2.40	0.80	68.67	5+
(UNMODIFIED)				287.10	2.08	0.40	81.73	
				384.88	2.28	0.32	86.53	
LIX 1104	20	50	20	98.59	4.04	2.92	30.61	3+
(MODIFIED)				194.70	3.92	3.00	25.77	
				291.80	3.96	2.56	37.94	
				389.15	3.92	2.44	39.62	
LIX 1104	20	25	20	195.13	2.40	1.44	42.40	5+
(MODIFIED)				289.10	2.08	1.04	52.00	
				382.98	2.28	0.72	69.68	
VERSATIC	20	50	20	101.82	4.04	3.60	14.46	3+
ACID				195.44	3.92	3.64	10.86	
				291.55	3.96	3.76	8.85	
				388.90	3.92	3.60	10.92	
KELEX 100	20	25	20	159.86	2.16	2.04	15.00	5+
				251.95	2.08	2.08	13.00	
				345.89	2.24	2.04	19.86	

Table 3.3. Antimony Extraction by Various Extractants at Variable Acidity and Temperature.

Extractant	Vol. %	Temp. (C)	time (min.)	sample [H2SO4] g/L	feed [Sb] g/L	sample [Sb] g/L	% Sb Extracted
TBP	100	50	20	102.31	0.102	0.102	10.00
				198.26	0.104	0.102	13.69
				275.61	0.102	0.104	12.31
				377.44	0.093	0.106	4.26
TBP	100	25	20	99.87	0.099	0.098	8.93
				194.84	0.099	0.090	10.00
				273.65	0.099	0.098	11.90
				359.32	0.099	0.099	15.00
TBP	100	50	20	202.88	0.402	0.313	29.93
				293.94	0.153	0.156	10.27
				376.94	0.231	0.251	6.55
TBP	100	25	20	195.96	0.402	0.408	8.66
				281.97	0.153	0.155	12.88
				358.48	0.231	0.236	14.18
DPPP	100	50	20	99.83	0.099	0.102	5.21
				192.71	0.099	0.106	2.57
				274.91	0.099	0.105	4.55
				353.14	0.099	0.106	5.78
DPPP	100	50	20	97.59	0.099	0.102	6.24
				187.11	0.099	0.108	2.91
				269.86	0.099	0.107	5.97
				348.34	0.099	0.108	7.27
DPPP	100	25	20	184.86	0.280	0.284	9.73
				266.56	0.127	0.136	7.91
				346.26	0.177	0.195	7.46
CYANEX 925	100	25	20	151.05	0.280	0.165	47.55
				229.16	0.127	0.120	16.85
				313.33	0.177	0.170	15.48
CYANEX 923	100	50	20	69.03	0.102	0.075	35.29
				138.05	0.104	0.079	34.67
				213.44	0.102	0.077	35.53
				288.83	0.093	0.074	29.98
CYANEX 923	75	50	20	79.80	0.102	0.086	23.27
				152.74	0.104	0.085	26.44
				231.06	0.102	0.080	29.41
				315.75	0.093	0.078	24.52
CYANEX 923	100	25	20	67.05	0.099	0.078	29.88
				132.36	0.099	0.075	32.58
				211.09	0.099	0.076	32.44
				292.54	0.099	0.072	36.75

CYANEX 923	100	25	20	132.48	0.280	0.195	41.50
				210.51	0.127	0.091	38.38
				291.74	0.177	0.129	37.32
DBBP	100	50	20	99.87	0.102	0.106	11.67
				185.54	0.104	0.107	14.61
				264.84	0.102	0.105	19.71
				341.70	0.093	0.109	8.82
DBBP	100	25	20	99.83	0.099	0.104	12.81
				181.78	0.099	0.109	10.82
				262.74	0.099	0.109	13.02
				340.72	0.099	0.109	15.22
DBBP	100	25	20	180.22	0.402	0.428	13.76
				265.76	0.153	0.160	17.39
				334.40	0.231	0.241	19.67
CYANEX 302	25	50	20	120.69	0.102	0.090	16.18
				211.34	0.104	0.070	34.71
				308.68	0.102	0.080	24.71
				402.31	0.093	0.090	5.16
M2EHPA	50	50	20	116.97	0.102	0.005	95.44
				201.65	0.104	0.003	97.32
				299.25	0.102	0.005	95.44
				392.62	0.093	0.006	93.94
LIX 1104	20	50	20	107.03	0.102	< .002	98.12
(UNMODIFIED)				198.92	0.104	< .002	98.15
				297.51	0.102	< .002	98.12
				390.64	0.093	< .002	97.94
LIX 1104	20	25	20	193.84	0.397	< .002	99.53
(UNMODIFIED)				287.10	0.142	< .002	98.66
				384.88	0.211	< .002	99.09
LIX 1104	20	50	20	98.59	0.099	0.004	96.12
(MODIFIED)				194.70	0.099	0.002	98.04
				291.80	0.099	0.002	98.06
				389.15	0.099	0.002	98.04
LIX 1104	20	25	20	195.13	0.397	0.003	99.27
(MODIFIED)				289.10	0.142	0.002	98.65
				382.98	0.211	0.004	98.18
VERSATIC	20	50	20	101.82	0.099	0.094	8.85
ACID				195.44	0.099	0.101	2.06
				291.55	0.099	0.097	5.94
				388.90	0.099	0.096	5.94
KELEX 100	20	25	20	159.86	0.280	0.023	92.61
				251.95	0.127	0.042	71.23
				345.89	0.177	0.126	37.36

Table 3.4. Bismuth Extraction by Various Extractants at Variable Acidity and Temperature.

Extractant	Vol. %	Temp. (C)	time (min.)	sample [H2SO4] g/L	feed [Bi] g/L	sample [Bi] g/L	% Bi Extracted
TBP	100	50	20	102.31	0.0085	0.0088	6.82
				198.26	0.0064	0.0064	12.00
				275.61	0.0048	0.0064	~0
				377.44	0.0064	0.0080	~0
TBP	100	25	20	99.87	0.0064	0.0056	19.50
				194.84	0.0072	0.0069	13.75
				273.65	0.0061	0.0051	25.59
				359.32	0.0056	0.0061	7.41
TBP	100	50	20	202.88	0.1930	0.1930	10.00
				293.94	0.1700	0.1860	3.72
				376.94	0.1730	0.2000	0.58
TBP	100	25	20	195.96	0.1930	0.2080	3.01
				281.97	0.1700	0.1890	4.39
				358.48	0.1730	0.1990	3.38
DPPP	100	50	20	99.83	0.0064	0.0077	~0
				192.71	0.0072	0.0085	~0
				274.91	0.0061	0.0074	~0
				353.14	0.0056	0.0064	~0
DPPP	100	25	20	97.59	0.0064	0.0075	~0
				187.11	0.0072	0.0077	4.82
				269.86	0.0061	0.0075	~0
				348.34	0.0056	0.0062	5.89
DPPP	100	25	20	184.86	0.1840	0.1920	7.13
				266.56	0.1700	0.1810	8.44
				346.26	0.1730	0.1920	6.77
CYANEX 925	100	25	20	151.05	0.1840	0.1480	28.41
				229.16	0.1700	0.1730	10.45
				313.33	0.1730	0.1810	7.93
CYANEX 923	100	50	20	69.03	0.0085	0.0059	38.92
				138.05	0.0064	0.0064	14.00
				213.44	0.0048	0.0056	0.37
				288.83	0.0064	0.0048	34.00
CYANEX 923	75	50	20	79.80	0.0085	0.0083	11.14
				152.74	0.0064	0.0056	21.25
				231.06	0.0048	0.0053	0.62
				315.75	0.0064	0.0064	10.00
CYANEX 923	100	25	20	67.05	0.0064	0.0064	11.00
				132.36	0.0072	0.0062	23.36
				211.09	0.0061	0.0067	3.34
				292.54	0.0056	0.0058	9.89

CYANEX 923	100	25	20	132.48	0.1840	0.1650	24.67
				210.51	0.1700	0.1580	20.07
				291.74	0.1730	0.1640	18.47
DBBP	100	50	20	99.87	0.0085	0.0101	~0
				185.54	0.0064	0.0075	2.73
				264.84	0.0048	0.0061	0.88
				341.70	0.0064	0.0080	2.75
DBBP	100	25	20	99.83	0.0064	0.0070	9.22
				181.78	0.0072	0.0088	1.00
				262.74	0.0061	0.0086	~0
				340.72	0.0056	0.0062	14.75
DBBP	100	25	20	180.22	0.1930	0.2330	2.21
				265.76	0.1700	0.2140	0.55
				334.40	0.1730	0.2220	1.19
CYANEX 302	25	50	20	120.69	0.0085	< .0016	> 82.12
				211.34	0.0064	< .0016	> 75.75
				308.68	0.0048	< .0016	> 68.00
				402.31	0.0064	< .0016	> 75.50
M2EHPA	50	50	20	116.97	0.0085	< .0016	> 82.49
				201.65	0.0064	< .0016	> 76.75
				299.25	0.0048	< .0016	> 69.00
				392.62	0.0064	0.0032	> 53.00
LIX 1104	20	50	20	107.03	0.0085	< .0016	> 81.93
(UNMODIFIED)				198.92	0.0064	0.0008	88.00
				297.51	0.0048	0.0008	84.00
				390.64	0.0064	0.0037	44.50
LIX 1104	20	25	20	193.84	0.1940	0.0142	93.12
(UNMODIFIED)				287.10	0.1730	0.0568	68.81
				384.88	0.1740	0.0312	82.79
LIX 1104	20	50	20	98.59	0.0064	0.0037	44.50
(MODIFIED)				194.70	0.0072	0.0061	17.82
				291.80	0.0061	0.0056	11.87
				389.15	0.0056	0.0050	13.39
LIX 1104	20	25	20	195.13	0.1940	0.1410	30.23
(MODIFIED)				289.10	0.1730	0.1530	15.10
				382.98	0.1740	0.1730	4.55
VERSATIC	20	50	20	101.82	0.0064	0.0059	11.50
ACID				195.44	0.0072	0.0080	~0
				291.55	0.0061	0.0072	~0
				388.90	0.0056	0.0069	~0
KELEX 100	20	25	20	159.86	0.1840	0.1550	24.18
				251.95	0.1700	0.1610	17.61
				345.89	0.1730	0.1690	14.03

The solvating extractants all extracted arsenic (V) to a significant extent. Arsenic (III) was only weakly extracted by the solvating extractants. LIX 1104 (modified and unmodified) extracted arsenic (V) and arsenic (III) (weaker). Antimony was extracted by Cyanex 923 (weak), M2EHPA, LIX 1104 (modified and unmodified) and Kelex 100. Bismuth extraction was significant for Cyanex 302, M2EHPA and LIX 1104 (modified and unmodified). The summary list is contained in Table 3.5.

Table 3.5. Reagent Formulations that Showed Significant As, Sb or Bi Extraction.

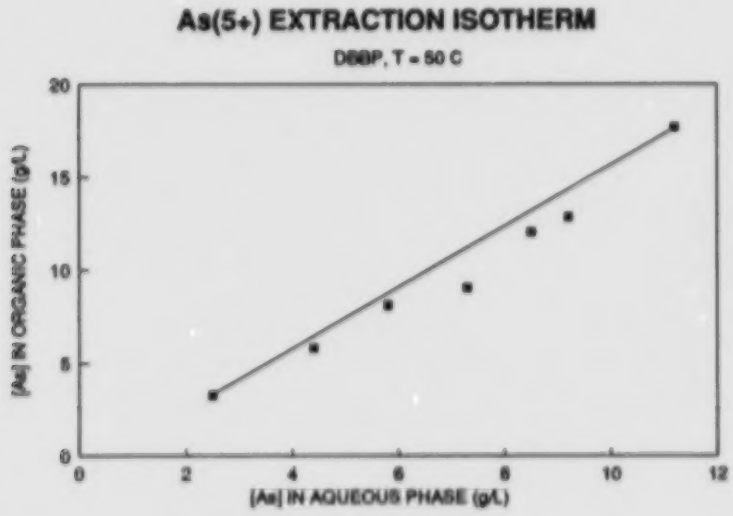
Extractant	Arsenic Extraction	Antimony Extraction	Bismuth Extraction
TBP	Yes		
DBBP	Yes		
DPPP	Yes		
Cyanex 923	Yes	Yes	
Cyanex 925	Yes		
LIX 1104 (unmodified)	Yes	Yes	Yes
LIX 1104 (modified)	Yes	Yes	Yes
M2EHPA		Yes	Yes
Kelex 100		Yes	
Cyanex 302			Yes

3.5 MCCABE THIELE DISTRIBUTION ISOTHERMS

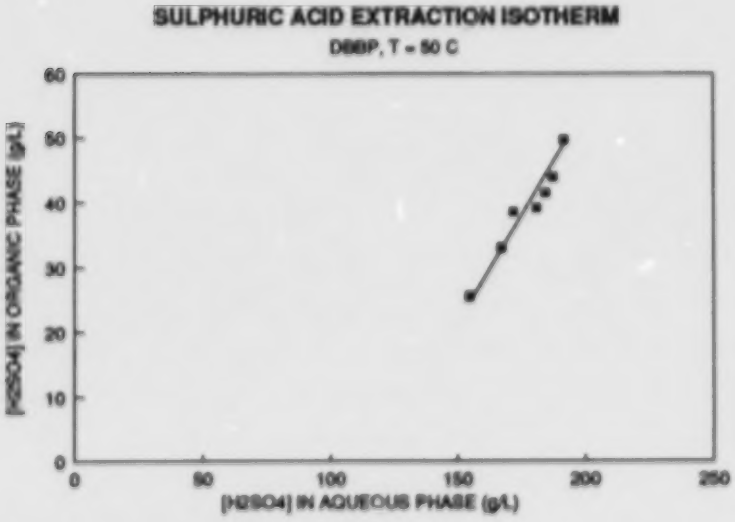
Additional shakeout tests were performed to generate McCabe-Thiele isotherms for the more promising systems listed in Table 3.5. Experiments were not conducted with TBP because of the extensive data that already exists for this system. LIX 1104 was excluded because of the reported difficulty of stripping this reagent (only pressure H_2S has been reported to strip As, Sb and Bi). Cyanex 302 was not investigated further because of the very strong extraction of copper by this reagent. Experiments with Kelex 100 were not successful and are therefore not reported. A third phase formed during extraction with Kelex 100. There was insufficient time available in the experimental program to obtain a modifier that would eliminate the third phase.

3.5.1 Arsenic Extraction

The distribution isotherms for arsenic extraction are shown in Figures 3.1 - 3.4. Also included in these figures for comparison are the distribution isotherms for sulphuric acid coextraction by the solvating extractants. Table 3.6 summarizes the ability of each solvent (TBP included) to separate arsenic from acid.

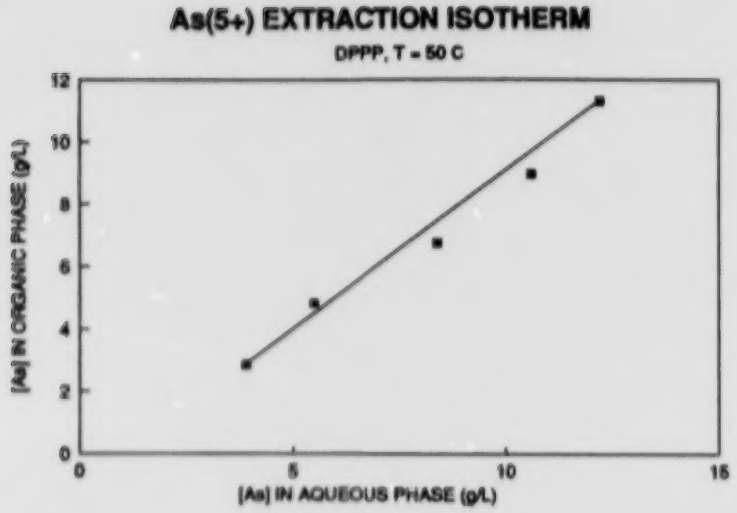


(a)

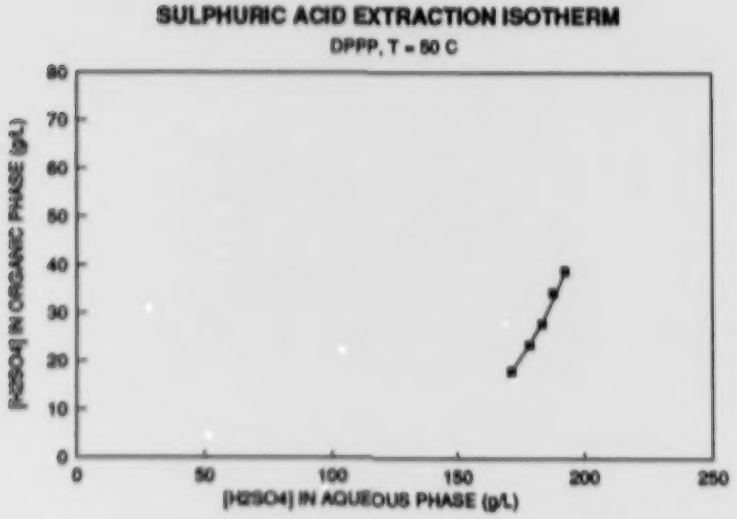


(b)

Figure 3.1 Distribution isotherm for (a) arsenic extraction and (b) acid extraction with DBBP.



(a)



(b)

Figure 3.2 Distribution isotherm for (a) arsenic extraction and (b) acid extraction with DPPP.

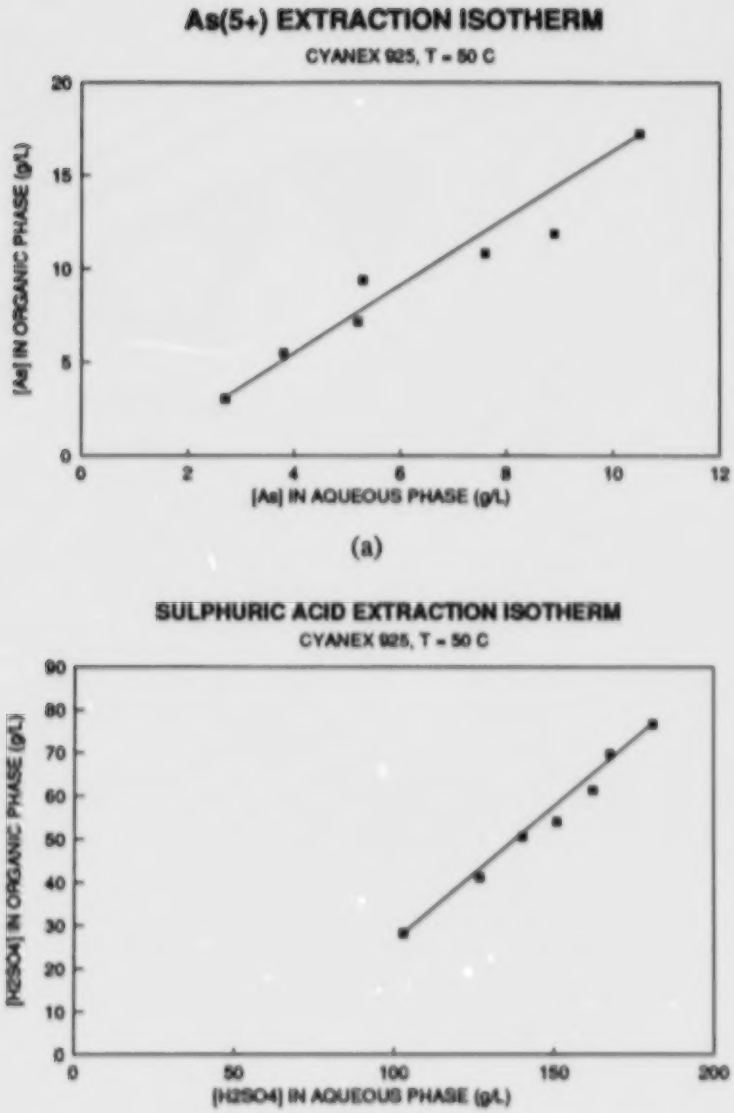
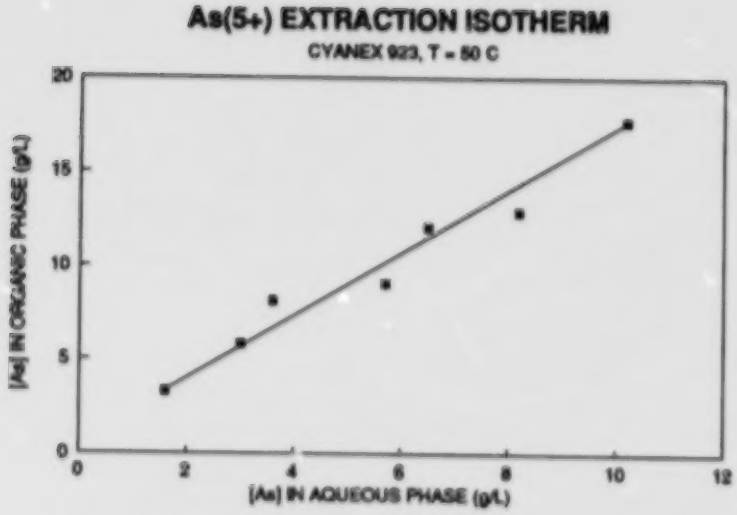
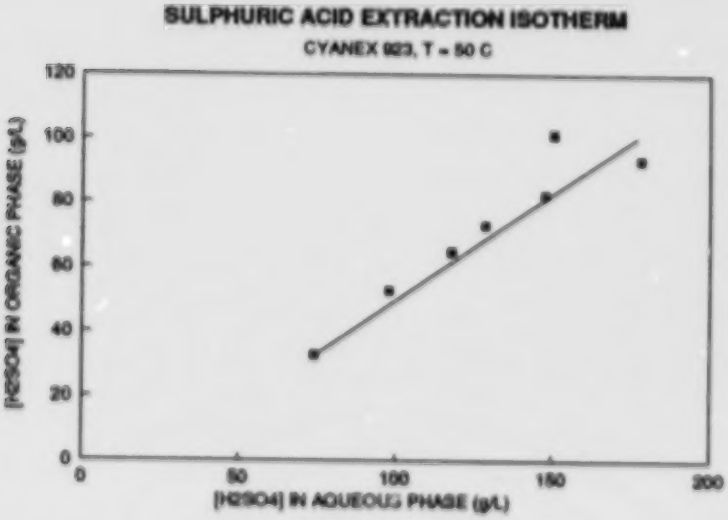


Figure 3.3 Distribution isotherm for (a) arsenic extraction and (b) acid extraction with Cyanex 925.



(a)



(b)

Figure 3.4 Distribution isotherm for (a) arsenic extraction and (b) acid extraction with Cyanex 923.

Table 3.6. The Separation of Arsenic and Acid by Solvating Extractants

Extractant	$[As]_{aq}$ (g/L)	$[As]_{org}$ (g/L)	D_{As}	$[H_2SO_4]_{aq}$ (g/L)	$[H_2SO_4]_{org}$ (g/L)	$D(H_2SO_4)$	$S(As/H_2SO_4)$
Cyanex 923	10.2	17.7	1.74	178	84.4	0.47	3.7
Cyanex 925	10.5	17.3	1.64	181	55	0.3	5.5
DBBP	11.2	14.6	1.30	192	38.7	0.2	6.5
DPPP	12.2	11.3	0.93	192	21.6	0.11	8.5
TBP	1.4	1.04	0.74	196	14.8	0.076	9.7

In general, the solvating extractants seem to extract arsenic (As(V)) in the following order of strength: phosphine oxides > phosphonates > phosphates. Unfortunately, the reagents that are stronger extractants for arsenic are also strong extractants for acid. TBP is superior to all other extractants in its ability to separate arsenic from acid. In an industrial application, the acid scrub requirement for TBP would therefore be expected to be less rigorous than for the other reagents studied. Of course, it is conceivable that arsenic may be removed from solutions where acid coextraction may be desirable.

3.5.2 Antimony Extraction

The antimony removal isotherms are shown in Figures 3.5-3.6. It is apparent that M2EHPA extracts antimony reasonably strongly. M2EHPA did not extract acid. Cyanex 923 is an inadequate extractant for antimony. As was the case for the arsenic extraction experiments, Cyanex 923 also co-extracted acid very strongly.

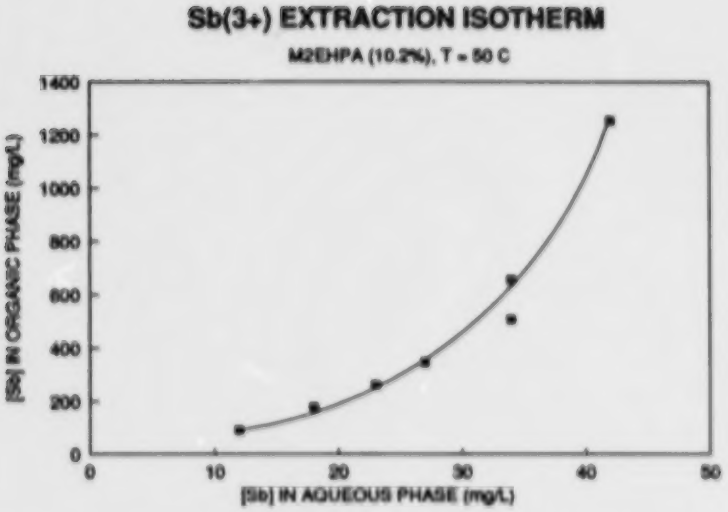


Figure 3.5 Distribution isotherm for antimony extraction with M2EHPA.

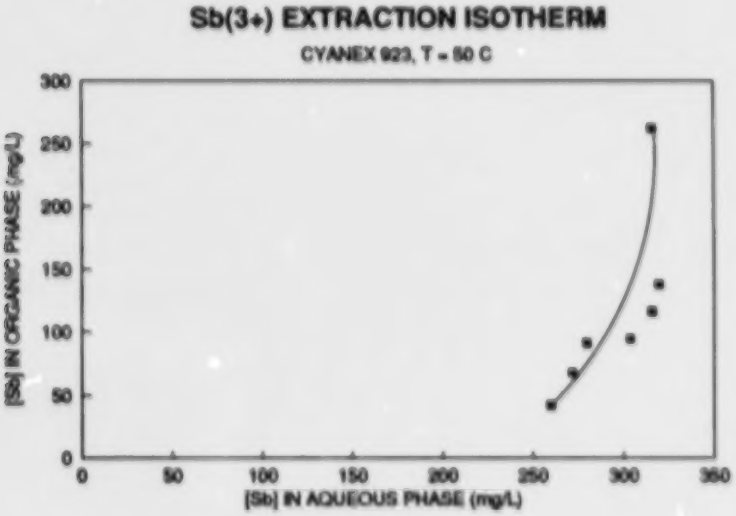


Figure 3.6 Distribution isotherm for antimony extraction with Cyanex 923.

3.5.3 Bismuth Extraction

The bismuth extraction isotherm is shown in Figure 3.7 indicates that M2EHPA extracts bismuth with good efficiency.

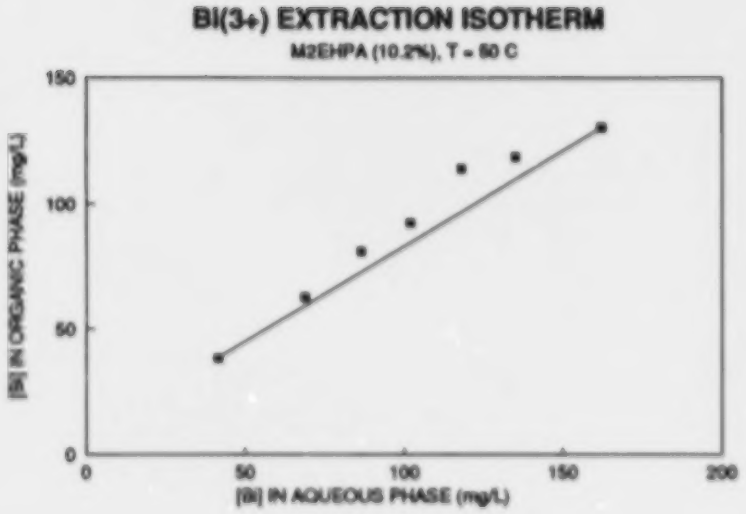


Figure 3.7 Distribution isotherm for bismuth extraction with M2EHPA.

3.5.4 Conclusions

The conclusions of the McCabe-Thiele work were the following:

1. Arsenic could be extracted by a wide range of solvating extractants. TBP was the weakest arsenic extractant but produced the best arsenic/acid separation. Other solvents were stronger in their arsenic extraction behaviour but also co-extracted more acid.

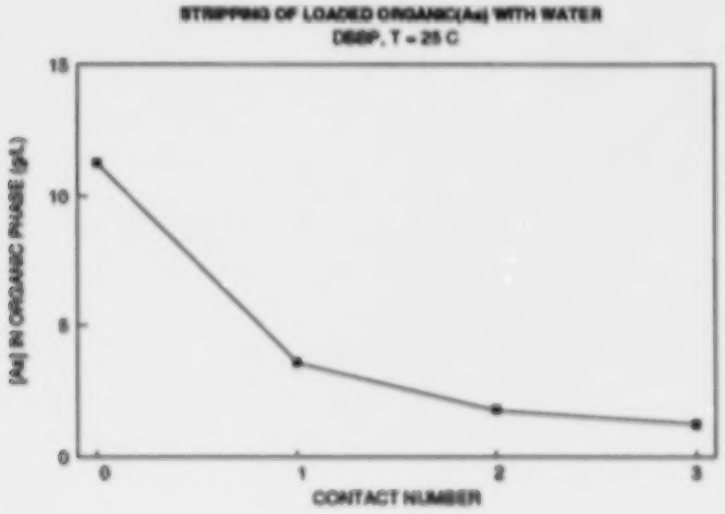
2. Antimony was extracted very strongly by M2EHPA. It is recommended that the extraction of antimony by M2EHPA be studied further. This is a promising reagent system.

3. Bismuth was extracted very strongly by M2EHPA. It is recommended that the extraction of bismuth by M2EHPA be studied further. This is a promising reagent system.

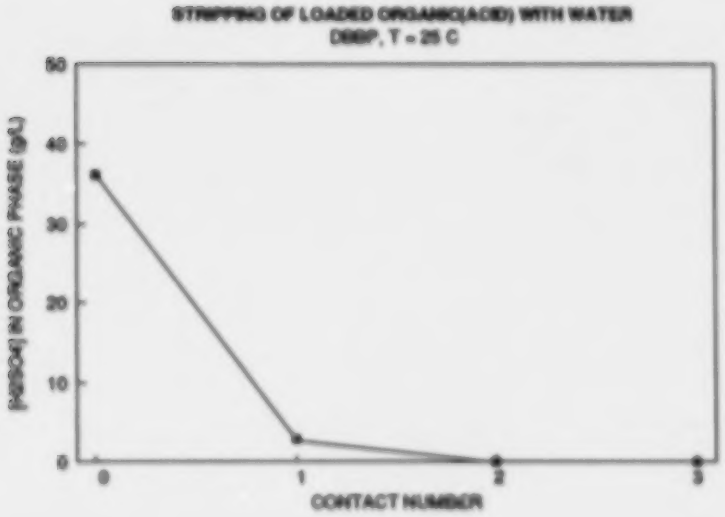
3.6 STRIPPING STUDIES

To determine whether it was possible to strip the impurities from the solvents after loading, a limited series of experiments was performed. Stripping studies were performed on metal-loaded solvents obtained in the McCabe-Thiele isotherm work reported in the previous section. The experimental procedure involved contacting the loaded solvent with the stripping reagent at an aqueous to organic ratio of 2:1 and at a temperature of 25 °C. Four sequential contacts were

performed. Each sample of aqueous strip solution was analyzed for its metal content. The metal content on the organic was calculated by mass balance techniques. Water was used to strip the solvating extractants. Sulphuric acid or hydrochloric acid were used to strip the acid extractants. The stripping experiments are summarized in Figures 3.8 to 3.14.

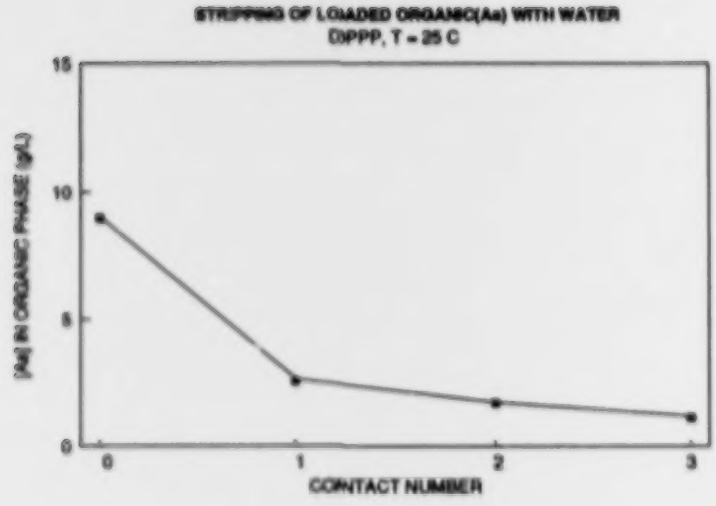


(a)

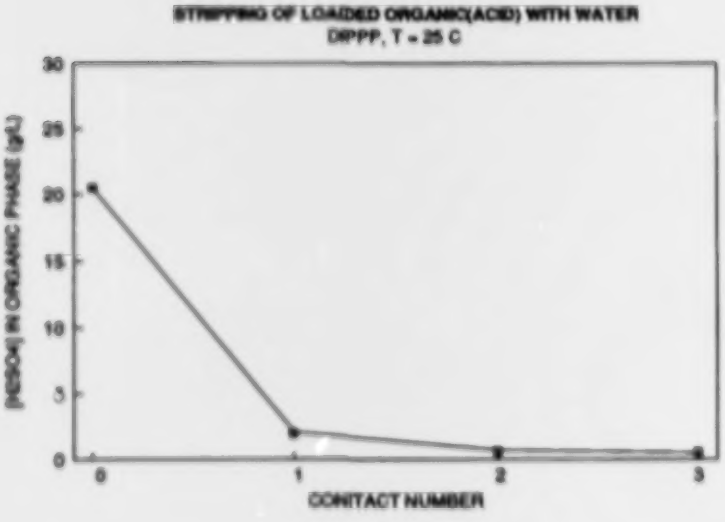


(b)

Figure 3.8 The stripping of (a) arsenic and (b) acid from DBBP.

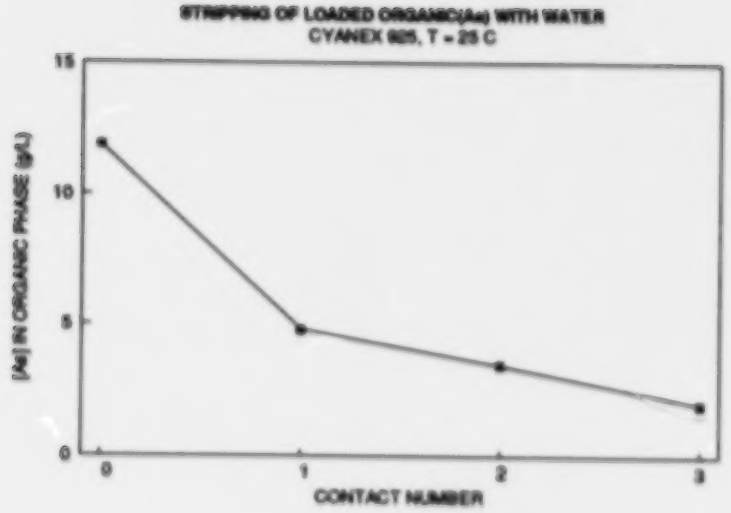


((a)

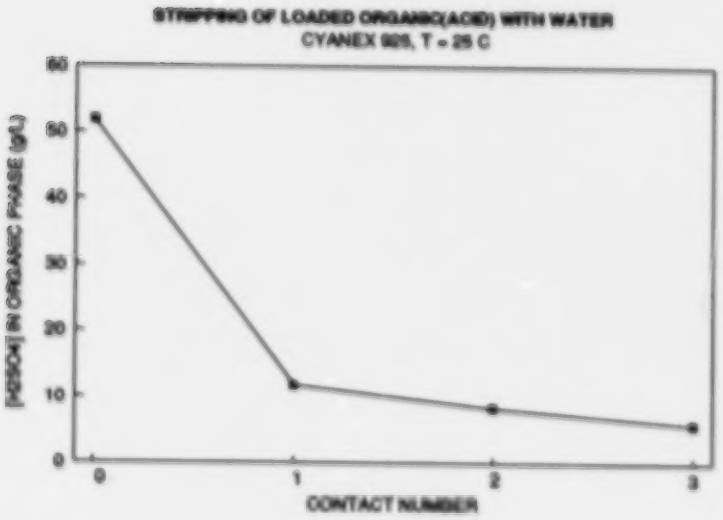


((b)

Figure 3.9 The stripping of (a) arsenic and (b) acid from DPPP.

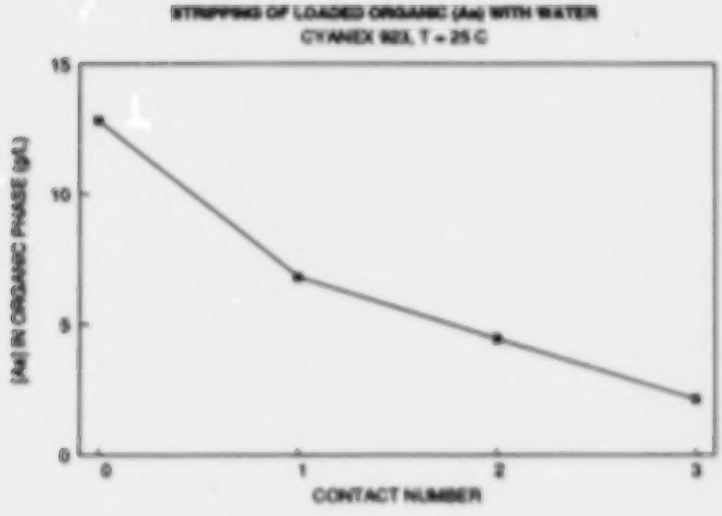


(a)

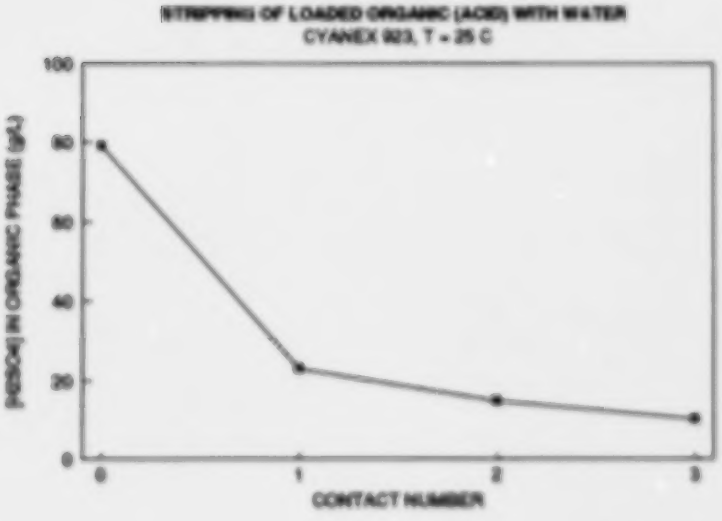


(b)

Figure 3.10 The stripping of (a) arsenic and (b) acid from Cyanex 925.



(a)



(b)

Figure 3.11 The stripping of (a) arsenic and (b) acid from Cyanex 923.

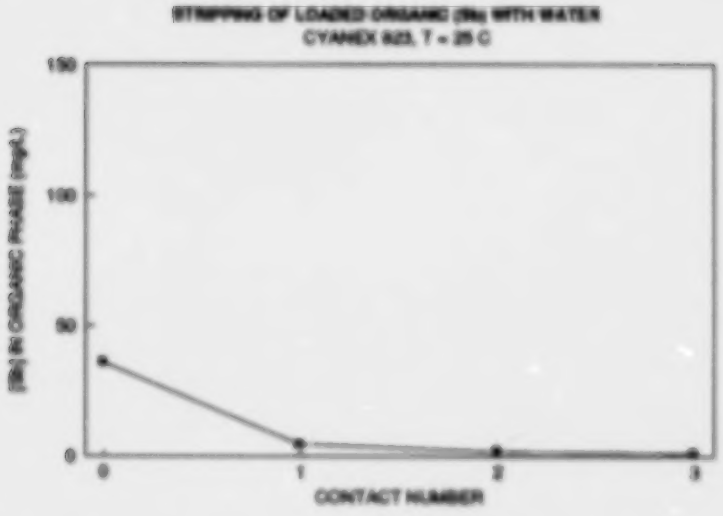
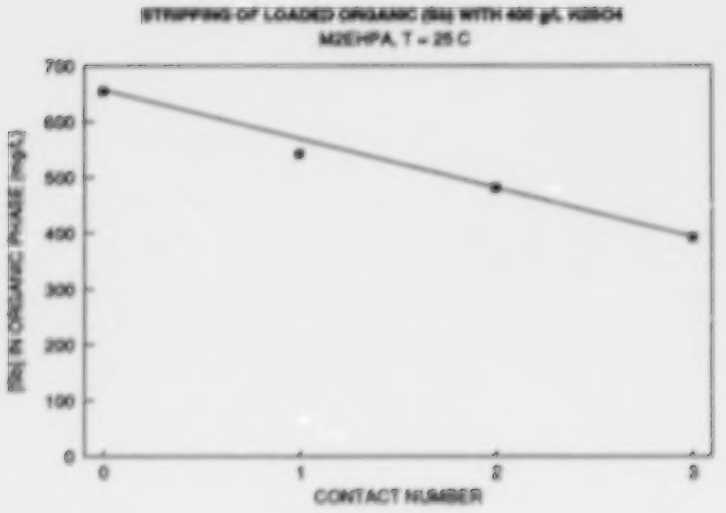
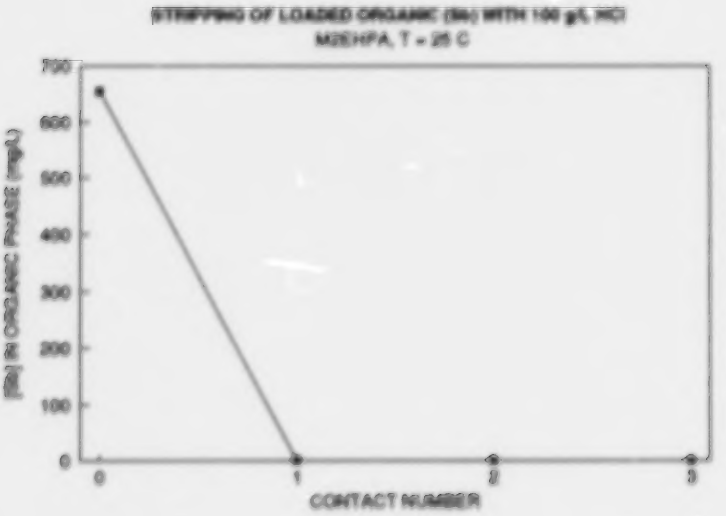


Figure 3.12 The stripping of antimony from Cyanex 923 with water.

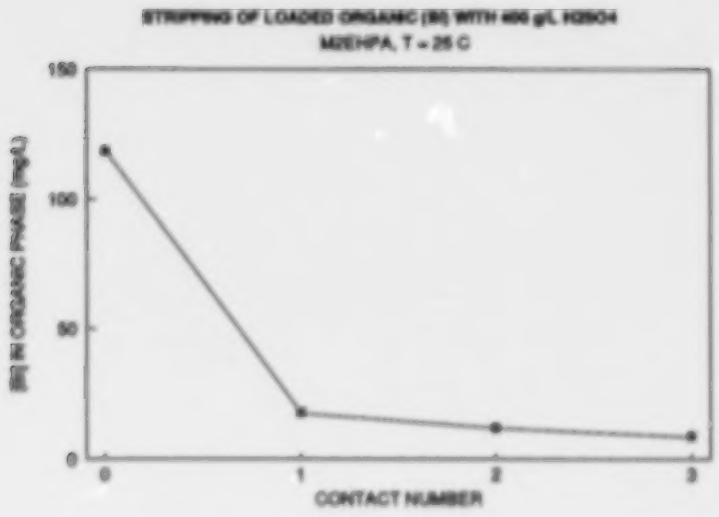


(a)



(b)

Figure 3.13 The stripping of antimony from M2EHPA with (a) 400 g/L H_2SO_4 and (b) 100 g/L HCl.



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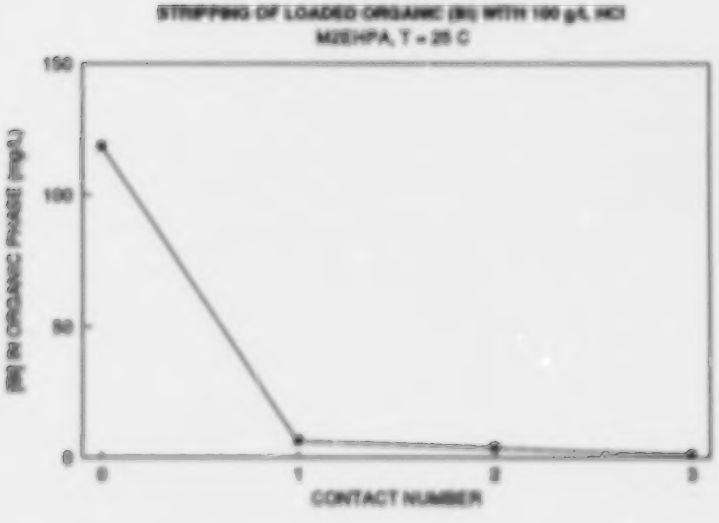


(b)

Figure 3.14 The stripping of bismuth from M2EHPA with (a) 400 g/L H_2SO_4 and (b) 100 g/L HCl.

The stripping of arsenic, antimony, bismuth and acid from the solvating extractants was demonstrated. The ease of arsenic stripping varied in the order DPPP > DBBP > Cyanex 925 > Cyanex 923. Antimony was easily stripped from Cyanex 923. Antimony stripping from M2EHPA with sulphuric acid was difficult. Hydrochloric acid stripped antimony from M2EHPA efficiently. Bismuth stripping from M2EHPA was accomplished with either hydrochloric or sulphuric acid.

4 ION EXCHANGE SCREENING EXPERIMENTS

Based on the literature review and discussions with reagent suppliers, various ion exchange resins were selected for laboratory study. The laboratory study was conducted in three stages. The first stage consisted of a series of shakeflask experiments in which a sample of resin was contacted with a sample of solution containing arsenic, antimony or bismuth. Secondly, column loading studies were completed using those resins that showed good impurity extraction in the shakeflask experiments. Lastly, the impurity metals were eluted from the columns.

4.1 EXPERIMENTAL METHODS

Synthetic electrolytes were prepared from reagent grade chemicals. $CuSO_4.5H_2O$ and concentrated H_2SO_4 were used to prepare the electrolyte matrix. As_2O_3 (arsenic (III)) or Na_2HAsO_4 (arsenic (V)) were dissolved in hot concentrated H_2SO_4 and added to the copper sulphate solution. Antimony was added as $Sb_2(SO_4)_3$. Bismuth was added as Bi_2O_3.

Ion exchangers were either used directly, rinsed with deionized water or conditioned with dilute acid to convert them into their acid form. Reagent manufacturers were consulted to determine the appropriate pretreatment.

Shakeflask experiments were similar to those used for the solvent extraction screening studies. 50 mL of solution was contacted with 5 g of resin at 50°C in 250 mL Erlenmeyer flasks. All solutions were prepared to contain copper (10 g/L) and sulphuric acid (200 g/L). Each impurity was studied in turn. The arsenic concentration (as arsenic (V)) was set at 2.5 g/L. Antimony was fixed at 0.4 g/L and bismuth at 0.2 g/L.

The column loading experiments were performed using 50 mL burettes equipped with externally mounted water jackets. 25 mL of ion exchange resin was placed into the burette. Water washing (upflow) was used to remove all air bubbles and fine resin particles from the resin bed. Temperature control was achieved by circulating water through the externally mounted water jacket. Solution containing the impurity elements was passed downflow through the column at a rate of 10 bed volumes per hour (250 mL per hour). The synthetic electrolyte used for column studies contained 30 g/L Cu, 200 g/L H_2SO_4 and the impurity of interest. The arsenic concentration (as arsenic(V)) was set at 15 g/L. Antimony and bismuth concentrations were 0.4 g/L and 0.2 g/L respectively. The solution was collected in sample bottles positioned below the burette outlet.

Column elution experiments were performed using the same apparatus as the column loading tests. Again, water washing (upflow) was used to remove electrolyte solution remaining in the bed and to resettle the resin bed prior to elution. The temperature was controlled at 25°C. Solution was again circulated through the bed at a rate of 10 bed volumes per hour.

4.2 ANALYTICAL TECHNIQUES

Aqueous samples collected from the shakeflask, loading and elution experiments were analysed for arsenic, antimony, bismuth and copper by flame atomic absorption spectrophotometry. Acid concentration was measured by titration with a base. Analytical procedures are identical to those described in the section on solvent extraction. Resin samples were not analyzed for metal content.

4.3 SHAKEFLASK EXPERIMENTS

A selection of resins was used in the shakeflask experiments. The ability of each resin to pick up each impurity was studied. Table 4.1 lists the resins included in this study.

Table 4.1. Resins Used in the Shakeout Tests.

Resin	Manufacturer	Functional Group	Resin Class
SP-112	Bayer	Sulfonic Acid	Strong Acid Exchanger
S-100	Bayer	Sulfonic Acid	Strong Acid Exchanger
TP-207	Bayer	Iminodiacetic Acid	Chelating Exchanger
OC-1026	Bayer	Di-2-ethyl-hexyl phosphoric acid	Solvent Impregnated Resin
OC-1014	Bayer	Tri-butyl phosphate	Solvent Impregnated Resin
XFS-4195.02	Dow	Picolamine	Chelating Exchanger
XFS-43084.00	Dow	Picolamine	Chelating Exchanger
Dowex 50W-X4	Dow	Sulphonic Acid	Strong Acid Exchanger
C-467	Rohm and Haas	Amino Phosphonic Acid	Chelating Exchanger
IRA-743	Rohm and Haas	N-methyl Glucamine	Weak Base
IRA-900	Rohm and Haas	Quaternary Amine	Strong Base Exchanger
IRC-718	Rohm and Haas	Imino Diacetic Acid	Chelating Exchanger
Chelex 100	BioRad	Imino Diacetic Acid	Chelating Exchanger
WACMP	ResinTech	Carboxylic Acid	Weak Acid
CG8-H+	ResinTech	Sulphonic Acid	Strong Acid Exchanger
CG10-H+	ResinTech	Sulphonic Acid	Strong Acid Exchanger
UR-3300	Unitika	Aminophosphonic Acid	Chelating Exchanger
Activated Carbon	Calgon	Type CPG	Not Applicable
TN-2328	Sherex	Hydroxyquinoline	Chelating Exchanger

4.3.1 Results

The results of the shakeout tests are summarized in Table 4.2. A number of resins showed promise as exchangers for arsenic, antimony and bismuth and Table 4.3 summarizes the most promising resins.

Table 4.2. Arsenic, Antimony and Bismuth Extraction Results using 5 g of Resin and 50 mL of Solution. Contact for 90 minutes at 50 °C.

Resin	Arsenic Extraction (%)	Antimony Extraction (%)	Bismuth Extraction (%)
SP-112	9	13	42
S-100	6	10	21
TP-207	18	34	28
OC-1026	6	15	13
OC-1014	17	23	33
XFS-4195.02	16	19	16
XFS-43084.00	30	40	35
Dowex 50W-X4	10	6	15
C-467	12	98	98
IRA-743	53	44	25
IRA-900	16	23	91
IRC-718	16	24	23
Chelex 100	--	25	22
WACMP	10	12	12
CG8-H+	11	13	22
CG10-H+	14	15	27
UR-3300	15	93	91
Activated Carbon	44	33	27
TN-2328	15	92	77

Table 4.3. Resins that Showed Significant Removal of Arsenic, Antimony or Bismuth in the Shakeout Tests.

Resin	Arsenic Extraction	Antimony Extraction	Bismuth Extraction
SP-112			Yes
Duolite C-467		Yes	Yes
IRA-743	Yes	Yes	
IRA-900			Yes
TN-2328		Yes	Yes
UR-3300		Yes	Yes

4.4 COLUMN LOADING EXPERIMENTS

The resin-impurity combinations listed in Table 4.3 were examined using column loading experiments. Each resin-impurity combination was examined in a single experiment. The results are presented in the following subsections.

4.4.1 Arsenic Extraction

The results of the column loading experiments for arsenic extraction with IRA-743 are shown in Figure 4.1. It is obvious that IRA-743 was very inefficient for extracting arsenic from these solutions. Breakthrough occurred very early. The loading of arsenic on IRA-743 was negligible.

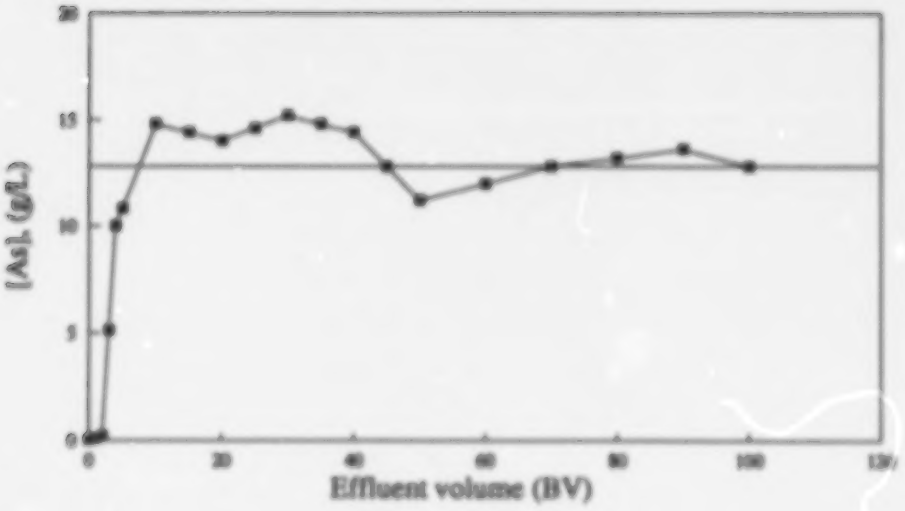


Figure 4.1. Adsorption of Arsenic on IRA-743. Conditions: Solution flow of 10 BV/hour, 50°C. Horizontal line indicates feed concentration.

4.4.2 Antimony Extraction

The results of the column loading experiments for antimony extraction are shown in Figures 4.2-4.5. IRA-743 had a rapid breakthrough of antimony. TN-2328 showed a mild extraction of antimony. UR-3300 was superior in performance to TN-2328. Duolite C-467 was superior to all other resins studied. Antimony was only beginning to breakthrough at 100 bed volumes. Maximum loading values are listed in Table 4.4.

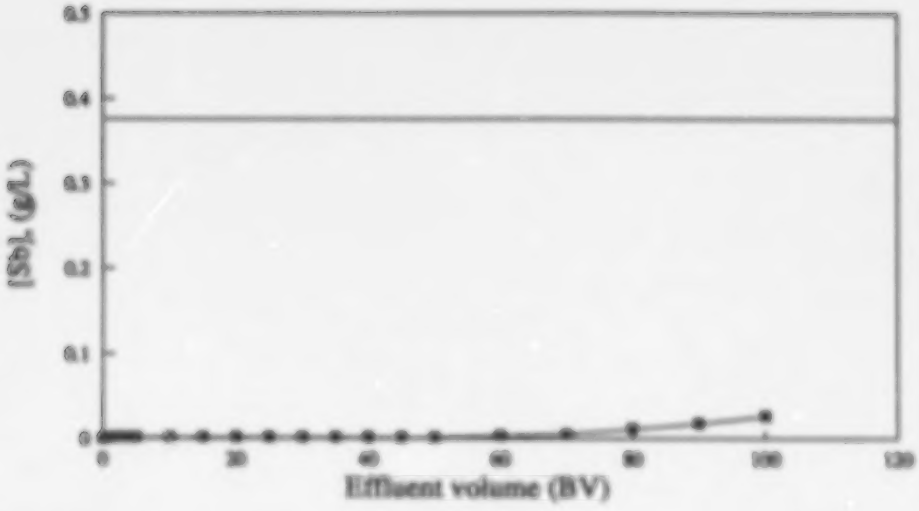


Figure 4.2. Adsorption of Antimony on C-467. Conditions: Solution flow of 10 BV/hour, 50°C. Horizontal line indicates feed concentration.

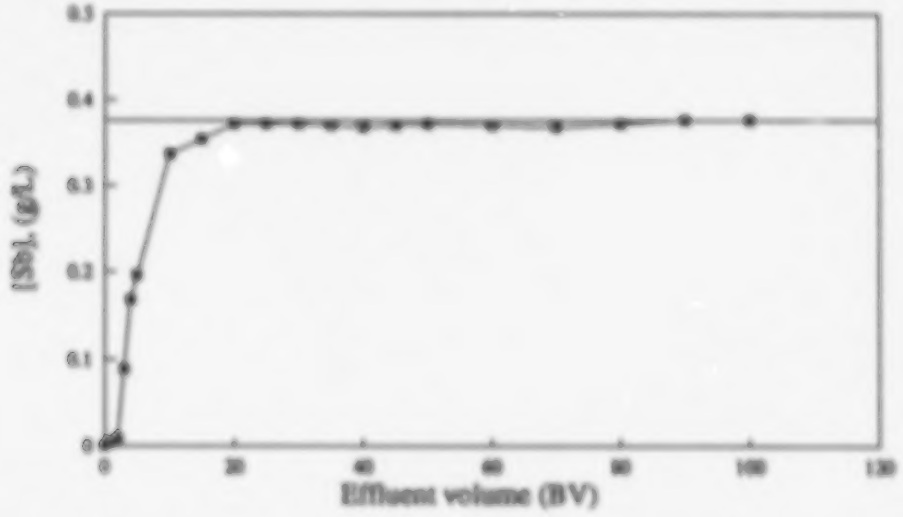


Figure 4.3. Adsorption of Antimony on IRA-743. Conditions: Solution flow of 10 BV/hour, 50°C. Horizontal line indicates feed concentration.

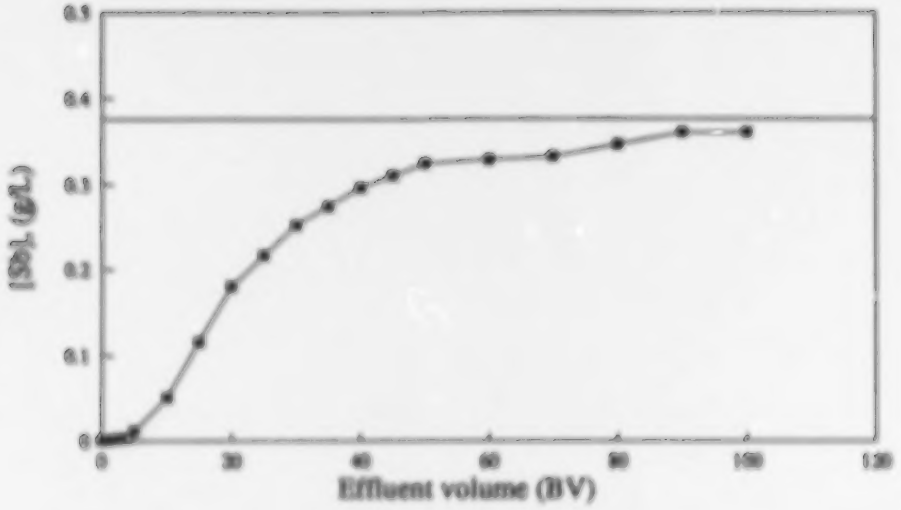


Figure 4.4. Adsorption of Antimony on TN-2328. Conditions: Solution flow of 10 BV/hour, 50°C. Horizontal line indicates feed concentration.

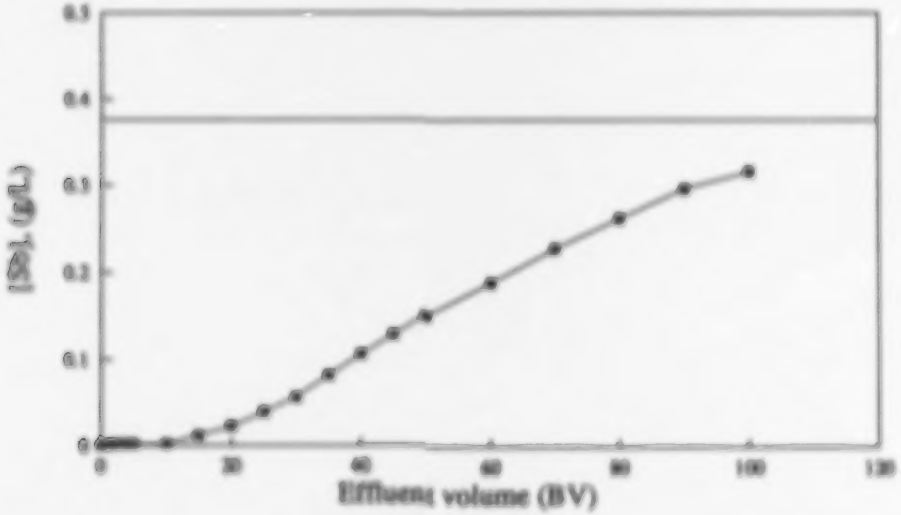


Figure 4.5. Adsorption of Antimony on UR-3300. Conditions: Solution flow of 10 BV/hour, 50°C. Horizontal line indicates feed concentration.

Table 4.4. Maximum loading values achieved in antimony loading experiments. These values were computed after 100 BV of solution were passed through the column.

Resin	Loading (g of Sb per liter of resin)
IRA-743	0.05
C-467	35.8
TN-2328	9.94
UR-3300	21.7

4.4.3 Bismuth Extraction

The results of the column loading experiments for bismuth extraction are shown in Figures 4.6-4.10. IRA-900 and SP-112 showed a rapid breakthrough of bismuth. TN-2328 showed a mild extraction of bismuth. UR-3300 was superior in performance to TN-2328. Duolite C-467 was superior to all other resins studied. As was the case for antimony, bismuth was only beginning to breakthrough at 100 bed volumes. Maximum loading values are listed in Table 4.5.

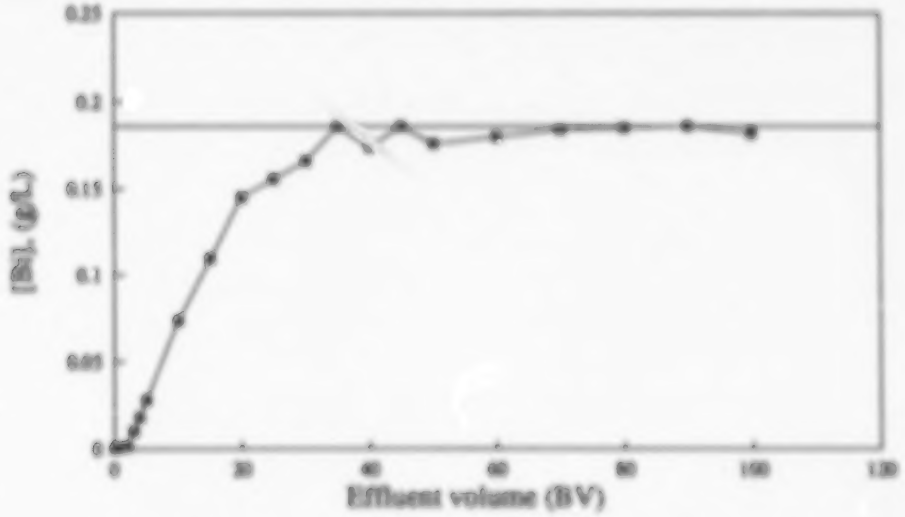


Figure 4.6. Adsorption of Bismuth on TN-2328. Conditions: Solution flow of 10 BV/hour, 50°C. Horizontal line indicates feed concentration.

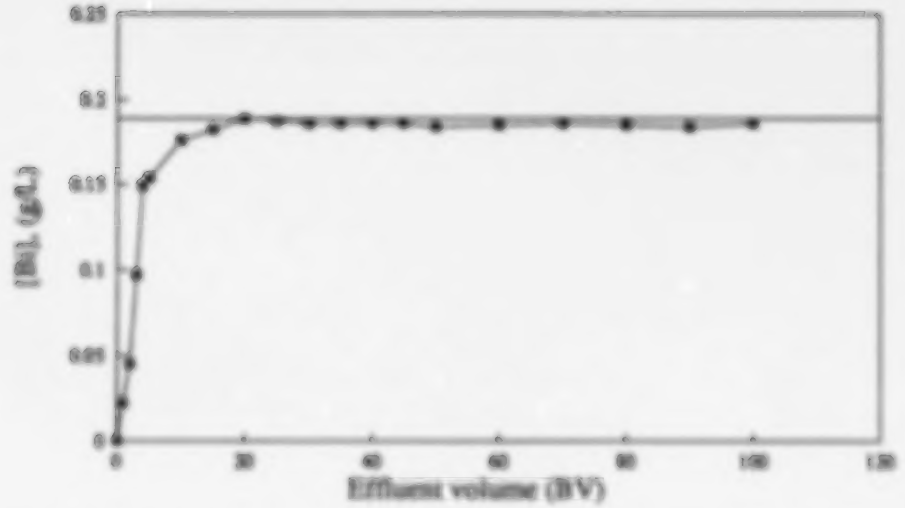


Figure 4.7. Adsorption of Bismuth on SP-112. Conditions: Solution flow of 10 BV/hour, 50°C. Horizontal line indicates feed concentration.

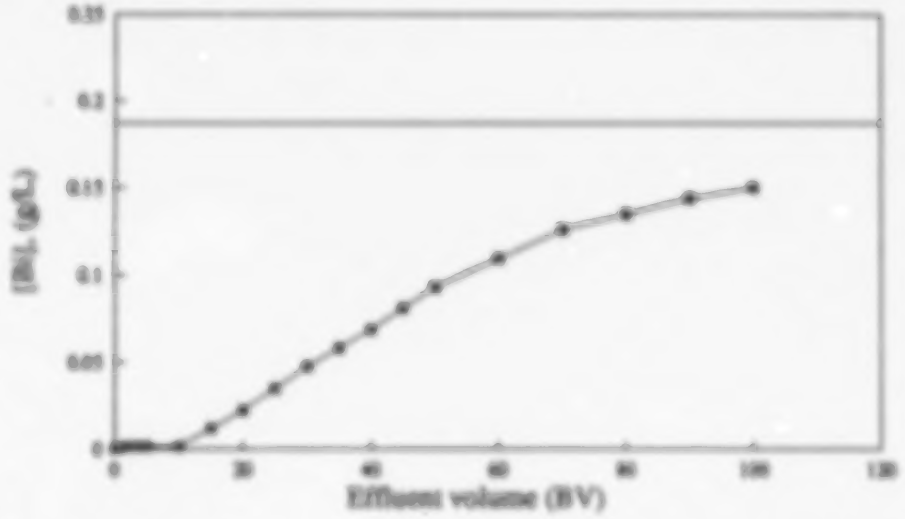


Figure 4.8. Adsorption of Bismuth on UR-3300. Conditions: Solution flow of 10 BV/hour, 50°C. Horizontal line indicates feed concentration.

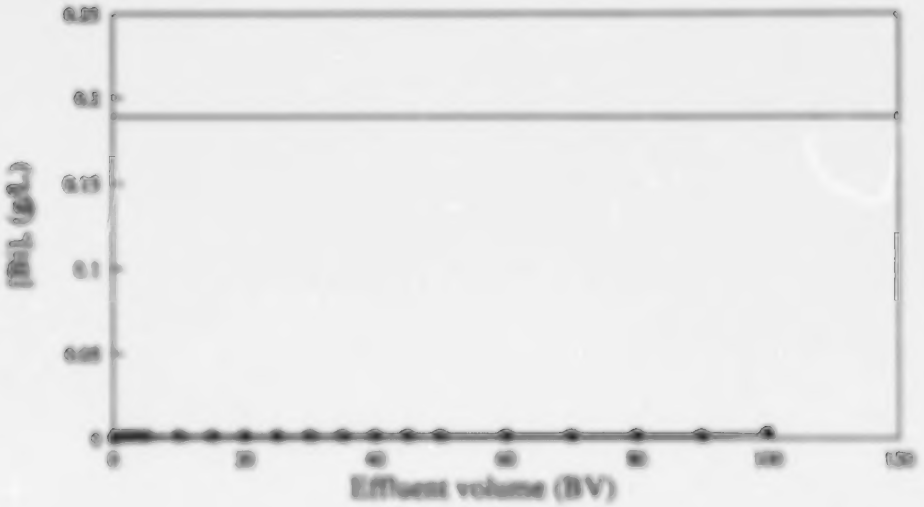


Figure 4.9. Adsorption of Bismuth on C-467. Conditions: Solution flow of 10 BV/hour, 50°C. Horizontal line indicates feed concentration.

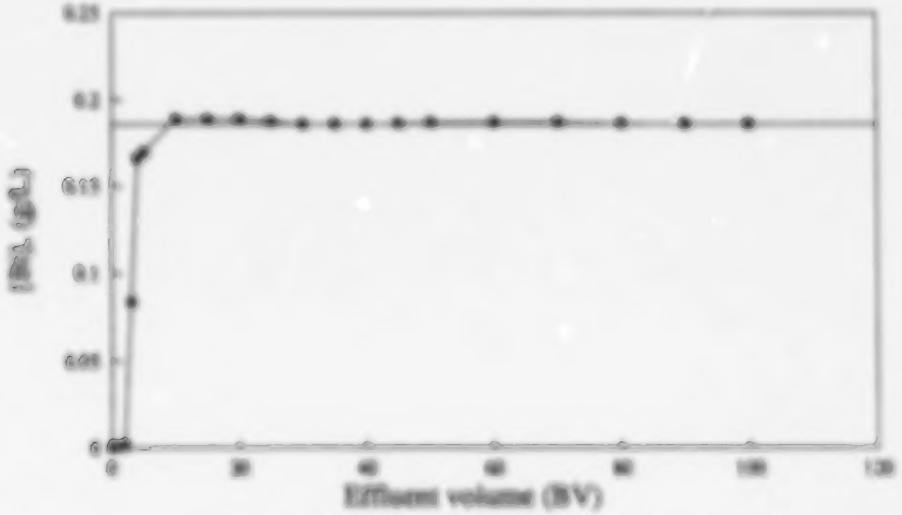


Figure 4.10. Adsorption of Bismuth on IRA-900. Conditions: Solution flow of 10 BV/hour, 50°C. Horizontal line indicates feed concentration.

Table 4.5. Maximum loadings achieved in bismuth loading experiments. These values were computed after 100 BV of solution were passed through the column.

Resin	Loading (g of Bi per liter of resin)
IRA-900	0.39
SP-112	0.84
C-467	19.24
TN-2328	2.16
UR-3300	9.77

4.5 COLUMN ELUTION EXPERIMENTS

To determine whether it is possible to elute the metals from the resins after loading, a limited number of elution experiments was conducted. Resin samples produced in the column loading work were retained for the elution studies. The choice of eluant was based on literature information or on discussions with reagent suppliers and users. In all cases the metals were quantitatively eluted from the resins.

4.5.1 Arsenic Elution

The elution of arsenic from IRA-743 is shown in Figure 4.11. Arsenic was essentially completely stripped in less than 10 BV of eluant. Unfortunately, the arsenic concentration of the eluant was always less than 2 g/L.

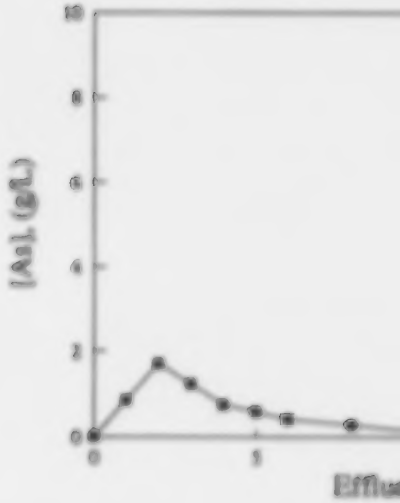
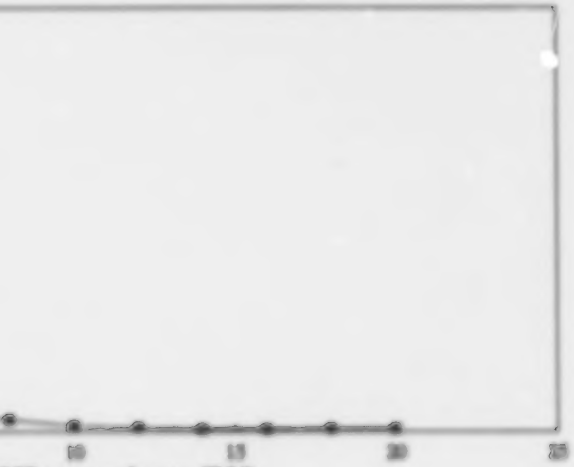


Figure 4.11. Elution of Arsenic from IRA-7
of 10 BV/hour, 25°C.

4.5.2 Antimony Elution

The antimony elution curves are shown
can be easily eluted from C-467 using a 10%
(Figure 4.3) only very weakly and therefore
TN-2328 was effectively eluted with 4M Na



IRA-743 with 10% (v/v) H_2SO_4. Conditions: Solution flow

shown in Figures 4.12-4.15. Figure 4.12 shows that antimony
a 10% HCl solution. Antimony was loaded onto IRA-743
refore did not show any response in elution (Figure 4.13).
M NaOH. UR-3300 was completely eluted using 6M HCl.

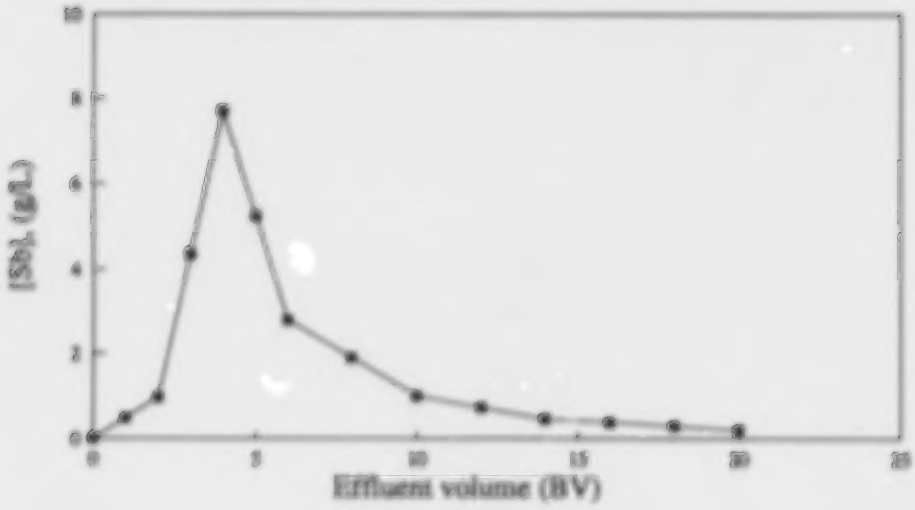


Figure 4.12. Elution of Antimony from C-467 with 10% (v/v) HCl. Conditions: Solution flow of 10 BV/hour, 25°C.

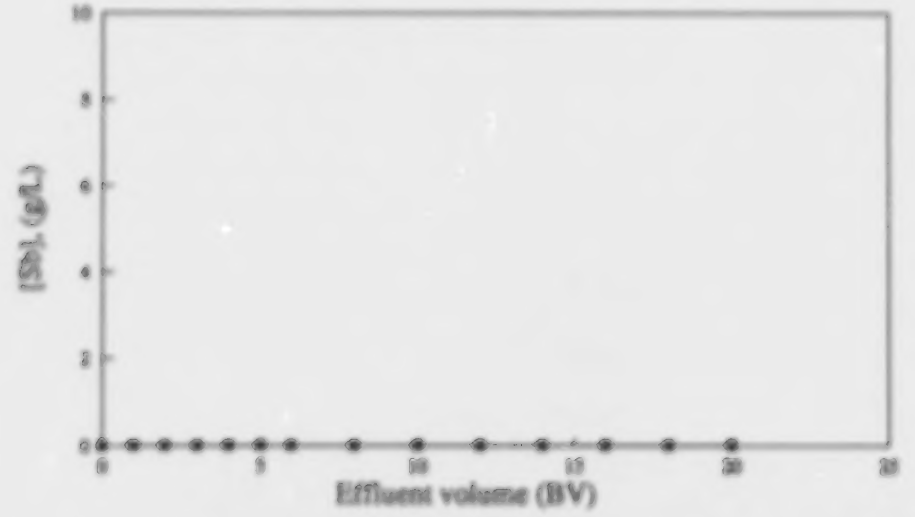


Figure 4.13. Elution of Antimony from IRA-743 with 10% (v/v) HCl. Conditions: Solution flow of 10 BV/hour, 25°C.

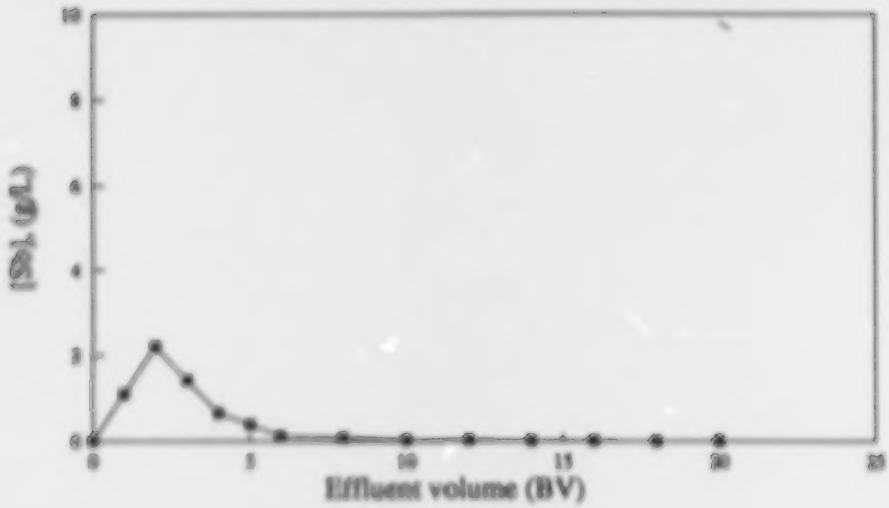


Figure 4.14. Elution of Antimony from TN-2328 with 4M NaOH. Conditions: Solution flow of 10 BV/hour, 25°C.

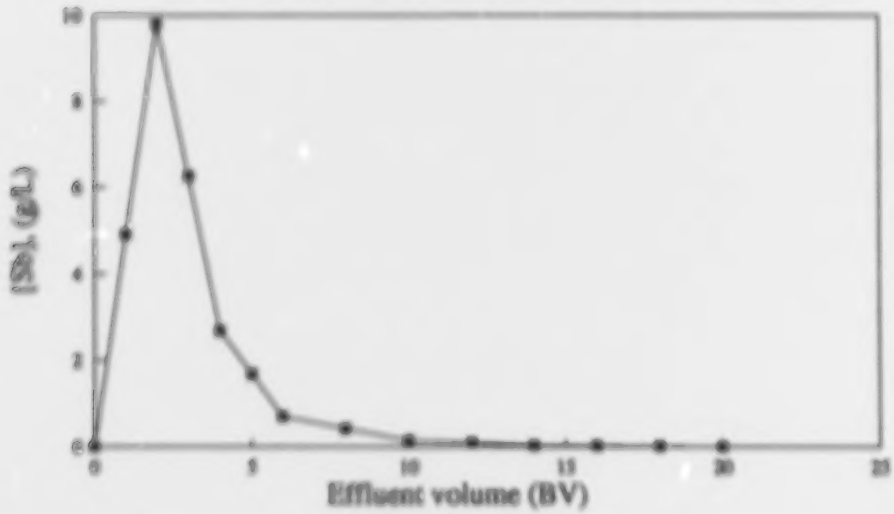


Figure 4.15. Elution of Antimony from UR-3300 with 6M HCl. Conditions: Solution flow of 10 BV/hour, 25°C.

4.5.3 Bismuth Elution

The bismuth elution results are reported in Figures 4.16-4.20. Bismuth was eluted from TN-2328 with 10% sulphuric acid. The elution proceeded slowly indicating that the kinetics of

stripping were poor. Bismuth was eluted from SP-112 with 10% HCl. 6M HCl was used to successfully elute bismuth from UR-3300. 10% HCl was used to elute bismuth from C-467. The loading of bismuth on IRA-900 was very low (Figure 4.10). Consequently, the stripping of bismuth from IRA-900 (Figure 4.20) showed a flat response.

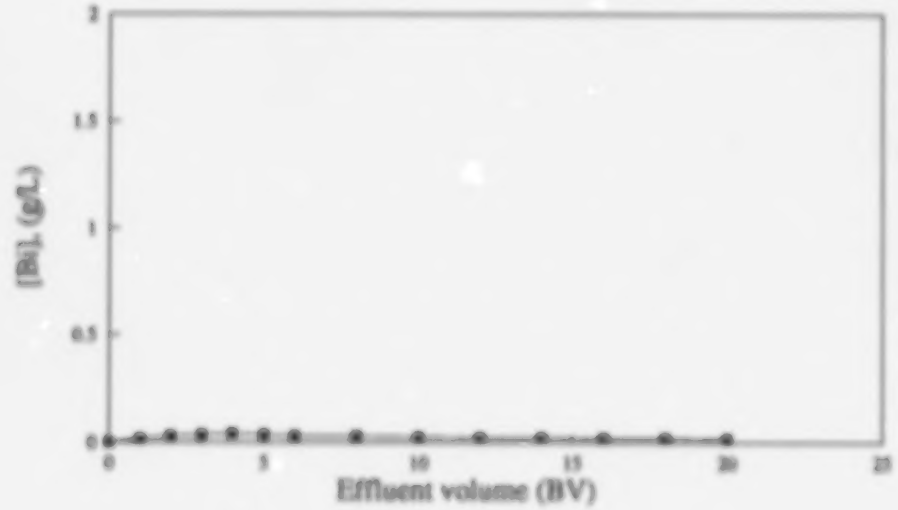


Figure 4.16. Elution of Bismuth from TN-2328 with 10% (v/v) H_2SO_4. Conditions: Solution flow of 10 BV/hour, 25°C.

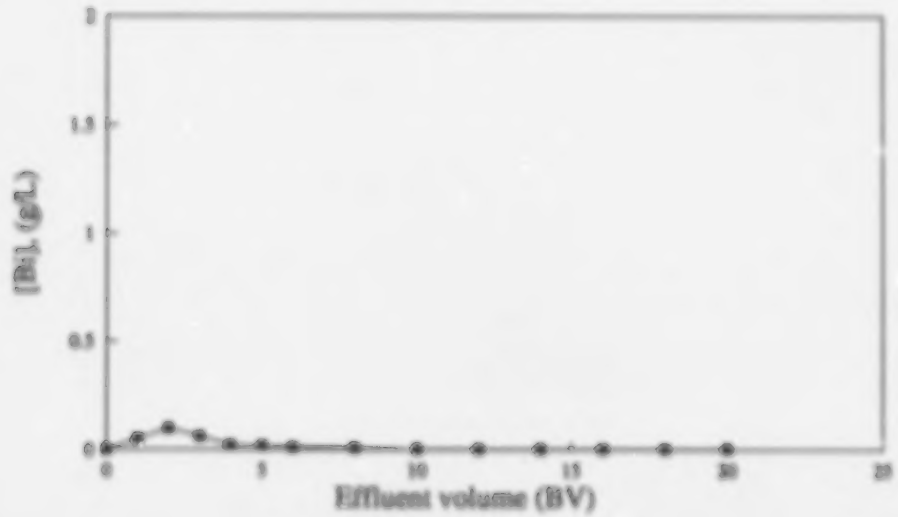


Figure 4.17. Elution of Bismuth from SP-112 with 10% (v/v) HCl. Conditions: Solution flow of 10 BV/hour, 25°C.

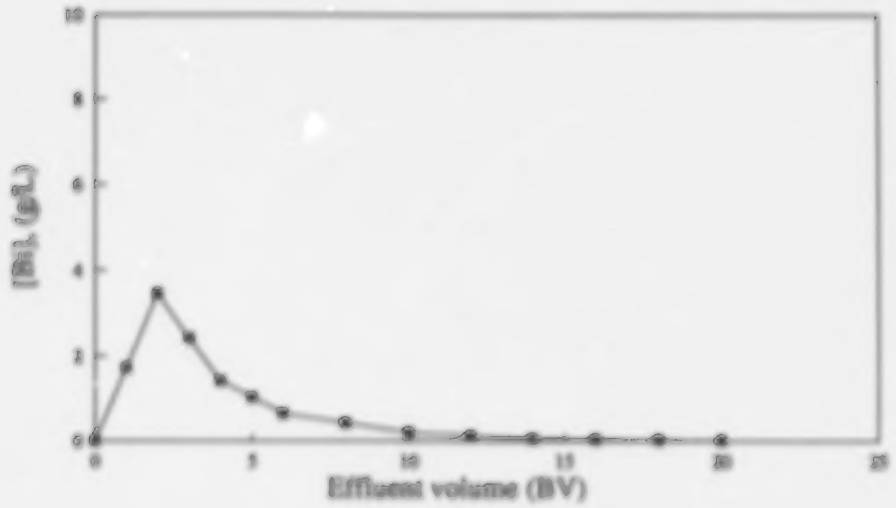


Figure 4.18. Elution of Bismuth from UR-3300 with 6M HCl. Conditions: Solution flow of 10 BV/hour, 25°C.

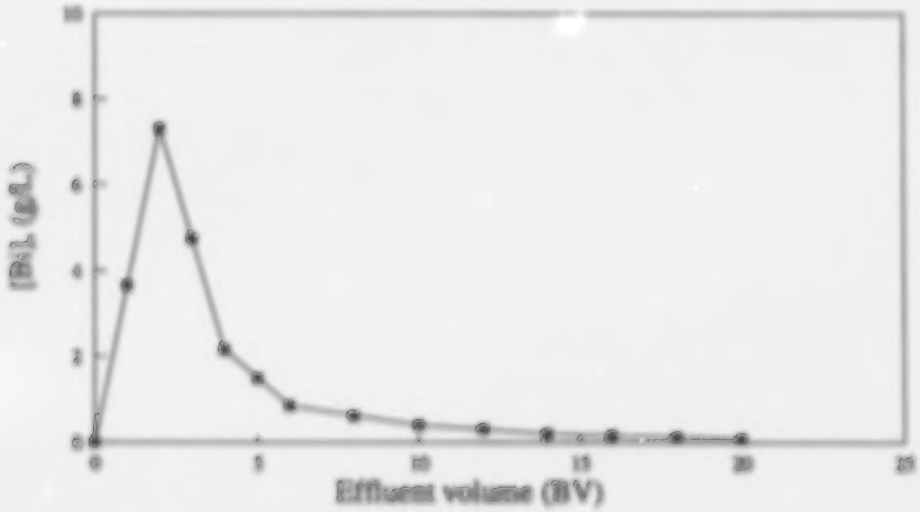


Figure 4.19. Elution of Bismuth from C-467 with 10% (v/v) HCl. Conditions: Solution flow of 10 BV/hour, 25°C.

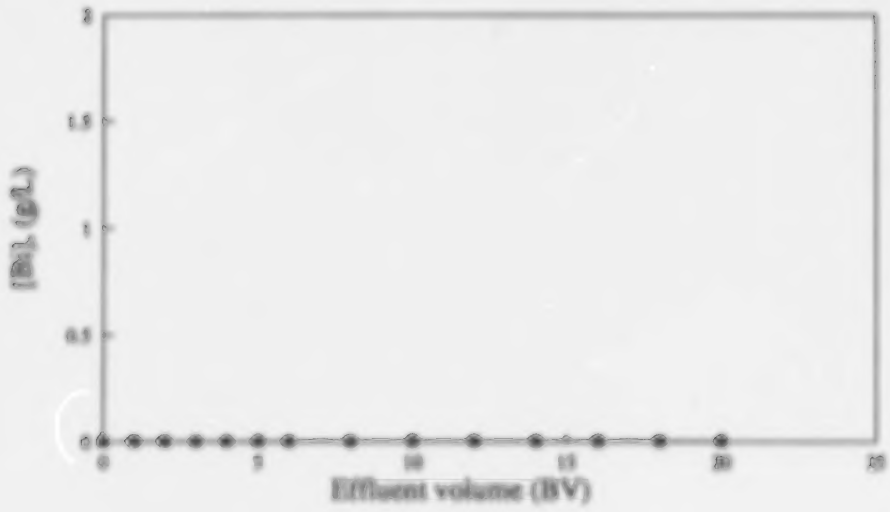


Figure 4.20. Elution of Bismuth from IRA-900 with 10% (w/v) NaCl. Conditions: Solution flow of 10 BV/hour, 25°C.

5 SUMMARY AND CONCLUSIONS

The following conclusions may be made following this survey of solvent extractants and ion exchangers.

1. Solvating extractants are capable of extracting arsenic from copper refinery electrolytes. The strength of the extractant for arsenic removal is linked to the strength of the extractant for acid extraction. Tri-butyl-phosphate is the most selective for arsenic over acid. Cyanex 923 is the strongest arsenic extractant identified in this study.

2. M2EHPA is a very good extractant for antimony and bismuth. Complete stripping of antimony and bismuth was demonstrated. The effective use of this reagent may be limited by reagent solubility in the aqueous phase and by the rate of hydrolytic degradation. Both of these issues should be discussed further with Albright and Wilson, the marketer of this reagent.

3. Hydroxamic acid extractants are very selective for arsenic, antimony and bismuth. Unfortunately, it is difficult to strip these species from the hydroxamic acid reagent after loading. These reagents are also prone to hydrolytic/oxidative degradation. Further development is required.

4. Kelex 100 is a promising reagent for antimony extraction. Unfortunately, in this work, a third phase developed during the studies with Kelex 100. Further investigations of antimony extraction and third phase appearance are required.

5. UR-3300 is selective for antimony and bismuth and can be stripped using 6M HCl. This resin is in use in a number of Japanese refineries, apparently with good success. Experiments included in this study confirmed the utility of this reagent.

6. C-467 is selective for antimony and bismuth and appears to be superior to UR-3300. These resins have similar functional groups. However, C-467 loaded antimony and bismuth to higher levels during standard tests. Breakthrough of antimony and bismuth did not occur until approximately the 100 bed volume mark.

7. TN-2328 is selective for antimony and loads bismuth weakly. However, this resin was inferior in performance to both UR-3300 and C-467. This resin falls in the developmental category. As such, it may be possible for Sherex to improve its functionality so that better performance is achieved.

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